

(Reprinted from *The Journal of the Society of Chemical Industry*, 31st May, 1890.  
No. 5, Vol. IX.)

## PHOTO-CHEMICAL INVESTIGATIONS AND A NEW METHOD OF DETERMINATION OF THE SENSITIVENESS OF PHOTOGRAPHIC PLATES

BY

FERDINAND HURTER, PH.D., AND V. C. DRIFFIELD.

---

### I. WHAT IS A PERFECT NEGATIVE? DENSITY, OPACITY, TRANSPARENCY.

THE production of a perfect picture by means of photography is an art; the production of a technically perfect negative is a science.

A perfect negative demands, in the first place, a perfect plate, and as the manufacture of dry sensitive plates is a large and rapidly-growing chemical industry, we need offer no apology for bringing this subject before this Society.

Our researches, which have covered a period of over ten years, were made with a view to rendering the production of perfect negatives as far as possible a matter of certainty.

What is a perfect negative? A negative is theoretically perfect when the amount of light transmitted through its various gradations is in inverse ratio to that which the corresponding parts of the original subject sent out.

The negative is mathematically the true inverse of the original when the opacities of its gradations are proportional to the light reflected by those parts of the original which they represent.

Before we can clearly understand this definition, it will be necessary to state shortly the laws of absorption of light by opaque black substances, and to define clearly the meaning we attach to the terms opacity, transparency and density of a negative. It is the more necessary to do this, as the whole of our investigations depend upon these laws.

For substances which do not reflect much light, such as black opaque bodies or transparent coloured bodies, the relation between the light absorbed

and the quantity of the substance present is very simple. If between the eye and a source of light we place a thin layer of dilute Indian ink, that layer absorbs light, and thereby reduces the intensity of the light transmitted. Assume that such a layer absorbs one-half of the light, then one-half of the light will be transmitted. Whatever may be the intensity of the original light, the intensity after passing this layer of ink will be one-half of what it was. The interposition of two such layers will reduce the light to one-quarter the original intensity; three such layers will reduce it to one-eighth, and so on, each layer reducing the intensity to one-half of what it receives.

Had the first layer allowed one-third of the light to pass through, then two such layers would reduce the intensity to one-ninth, three layers to one-twenty-seventh, &c. In general any number of layers would reduce the intensity of the light to a fraction, which is equal to the fraction the first layer allows to pass, but raised to a power, the index of which is the number of layers employed. If  $n$  equal layers were employed, and the first one reduced the intensity of the light to a fraction  $\frac{I}{m}$ , the  $n$  layers would reduce it to  $\left(\frac{I}{m}\right)^n$ .

If instead of using so many successive layers, the first layer were made to contain as much Indian ink as the  $n$  successive layers contain altogether, we should find that the one layer now reduces the intensity of light by exactly the same amount as the  $n$  layers did. The reduction of the intensity is, of course, due to the black particles, and depends simply upon the number of them which are interposed per unit of area. We can thus replace the number of layers by the number of particles, and the law takes this form:—The intensity  $I_x$  of light after passing  $A$  molecules of a substance is a fraction of the original intensity  $I$ , such that—

$$\frac{I_x}{I} = \left(\frac{I}{C}\right)^A$$

For purely mathematical reasons the fraction  $\frac{I}{C}$  is usually expressed as a negative power of the base of the hyperbolic logarithms  $\epsilon$ , say  $\frac{I}{C} = \epsilon^{-k}$  and we can write—

$$\frac{I_x}{I} = \epsilon^{-kA}.$$

where  $k$  is called the coefficient of absorption. This form of the law we shall frequently use again. The fraction  $\frac{I_x}{I}$  represents and measures the *transparency* of the substance. The inverse of that fraction, or  $\frac{I}{I_x} = \epsilon^{kA}$

measures the *opacity* of the substance. It indicates what intensity of light must fall on one side of the substance in order that unit intensity may be transmitted.

In our investigations we use the letter T to denote transparency, and O to denote opacity, and the two symbols are related thus:— $O \times T = 1$ .

We must further define what we mean by density as distinct from opacity. By density we mean the number of particles of a substance spread over unit area, multiplied by the coefficient of absorption;  $kA$  is what we term density, and mark by the letter D.

For our purposes, *i.e.*, in its application to negatives, the density is directly proportional to the amount of silver deposited per unit area, and may be used as a measure of that amount.

The relations between the three terms, transparency, opacity and density, are the following:—

$$T = e^{-D}$$

$$O = e^D$$

$$D = \log_e O = -\log_e T.$$

The density is the logarithm of the opacity, or the negative logarithm of the transparency.

These relations hold good for some substances with regard to ordinary white light, for others only with regard to monochromatic light, and for others they do not hold good at all. We have satisfied ourselves that they do hold good for the silver deposited as a black substance in negatives so long as the silver does not assume a metallic lustre, and reflects but a very small amount of light.

By means of these definitions we are now in a position to trace the connection between the densities of a theoretically perfect negative and the light intensities which produced them.

Since the density is the logarithm of the opacity, and since, in a theoretically perfect negative, the opacities are directly proportional to the intensities of the light which produced them, it follows that each density must be proportional to the logarithm of the light intensity which produced it. (More correctly, the density is a linear function of the logarithm of the intensity of light and time of exposure.)

The result is this:—In a theoretically perfect negative, the amounts of silver deposited in the various parts are proportional to the logarithms of the intensities of light proceeding from the corresponding parts of the object.

The question arises, can such a negative be produced in practice?

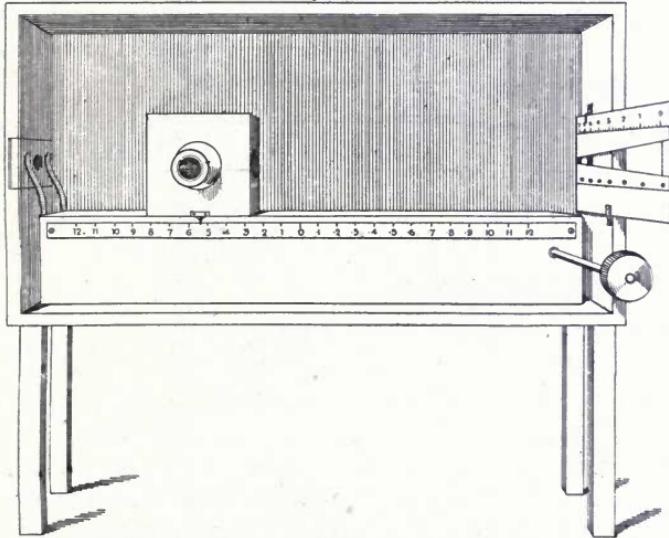
In order to answer this question, we had first to find a simple method of measuring the density of the silver deposited in negatives. We had then

to study the influence of the developers upon the density of the deposits, and we were then in a position to investigate the action of the light itself.

## II. INSTRUMENT FOR MEASURING DENSITIES.

We proceed to describe the instrument for measuring the density of the deposit. It is based on the relation existing between density and opacity. We measure the opacity of the plate, and in order to avoid calculations and references to tables of logarithms, the scale of the instrument is so arranged as to read the logarithm of the opacity, which is the density. The reason why we prefer to have the results expressed as density is because the density is a measure of the amount of silver deposited, or of the chemical work done by the light.

Fig. 1



*Hurter & Driffield's Apparatus for Measuring Density of Negatives*

The instrument pictured in Figs. 1 and 2 consists essentially of a small Bunsen photometer similar to those used for testing the illuminating power of gas, &c. The paper disc with its grease spot is placed in a small cubical chamber. The chamber carries an eye-piece, through which an image of each side of the disc can be viewed in two small mirrors, and so compared. The chamber can be made to slide in a straight line on a support by turning a key connected to one of two pulleys, over which passes an endless cord attached

to the chamber. This arrangement is placed within a larger box, the ends of which have apertures through which light is admitted from two powerful petroleum lamps. Corresponding exactly with these apertures, similar apertures are bored into the sides of the small chamber, which admit the light to either side of the Bunsen disc. The dimensions we have adopted are, for the larger box, 12 in. long, 6 in. high and 4 in. deep. The small chamber is a cube measuring 2 in. inside. We find it necessary to blacken everything within the box except the scales, and it is also important to exclude all extraneous light by means of a screen. The heat of the lamps also very soon injures the woodwork unless it is covered with asbestos cardboard and sheet metal.

Fig 2

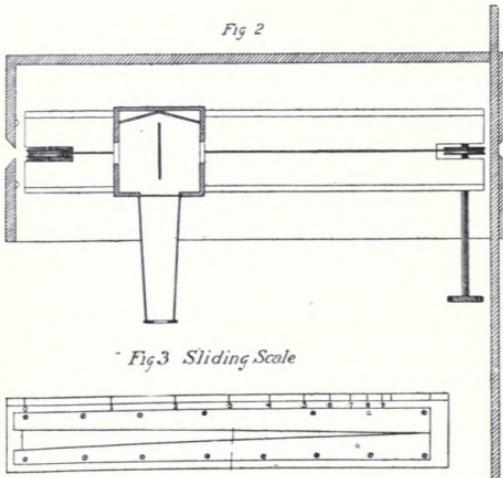


Fig 3 Sliding Scale



The aperture in the left-hand end of the large box we reduce to about  $\frac{1}{4}$  in. diameter by a diaphragm. At this end is placed the plate to be measured, held in position by springs. The hole at the right-hand end of the box is reduced by a rectangular diaphragm,  $\frac{1}{4}$  in. wide and  $\frac{1}{2}$  in. long, the length being vertical. This diaphragm can be reduced in length by moving a taper diaphragm past it.

The instrument is provided with two scales, one fixed, the other movable, the use and construction of which we will now explain. The fixed scale indicates the position of the disc chamber, and is constructed as follows:—

Suppose that the lamp on the left-hand side gives light of the intensity  $I_1$ , and that on the right-hand side light of intensity  $I_2$ , and that both lamps

are equidistant from the centre of the instrument, and that this distance is  $l$ . Then, when the disc chamber has been moved to a distance  $x$  from the centre of the instrument, so that—

$$(1) \quad \frac{I_1}{(l-x)^2} = \frac{I_2}{(l+x)^2} \text{ or } \frac{I_1}{I_2} = \left(\frac{l-x}{l+x}\right)^2$$

the two images of the disc will be alike. If a plate is now inserted, which reduces the light from the intensity  $I_1$  to intensity  $i$ , then the disc chamber will have to be moved to another place nearer to the plate before the two images of the disc are alike again. Supposing the distance of the disc from the centre of the instrument is now  $y$ , then—

$$(2) \quad \frac{i}{(l-y)^2} = \frac{I_2}{(l+y)^2} \text{ or } \frac{I_2}{i} = \left(\frac{l+y}{l-y}\right)^2$$

By multiplying the two equations we find the fraction, which measures the opacity—

$$\frac{I_1}{i} = \left(\frac{l-x}{l+x}\right)^2 \quad \left(\frac{l+y}{l-y}\right)^2$$

Taking logarithms on both sides, we have, since  $\log. \frac{I_1}{i}$  is the density  $D$  of the plate—

$$D = \log. \left(\frac{l+y}{l-y}\right)^2 - \log. \left(\frac{l+x}{l-x}\right)^2$$

If, therefore, at the distances  $x$  and  $y$  we write on the scale the values of  $\log. \left(\frac{l+x}{l-x}\right)^2$  and  $\log. \left(\frac{l+y}{l-y}\right)^2$  we can simply read off these logarithms, subtract one from the other, and the result is the density of the plate. For general convenience we use vulgar and not hyperbolic logarithms. In order to avoid all errors arising from the distance of the lamps, we make the apertures in the box small compared with the luminous portion of the flame of the lamps; it can be shown that in that case the distance  $l$  must be measured between the centre of the instrument and the diaphragm.

The following table gives the relative distances of the various points of the scale from the centre of the instrument, at which the logarithms of  $\left(\frac{l+x}{l-x}\right)^2$  have the values 0.1, 0.2, 0.3, &c.,  $l$  being half the distance between the diaphragms.

TABLE I.—*Fixed Scale of Instrument.*<sup>1</sup>

Log. $\left(\frac{l+x}{l-x}\right)^2$	Distance from centre of instrument.	Log. $\left(\frac{l+x}{l-x}\right)^2$	Distance from centre of instrument.
0.000	$l \times 0.000$	0.900	$l \times 0.476$
0.100	$l \times 0.057$	1.000	$l \times 0.519$
0.200	$l \times 0.114$	1.100	$l \times 0.560$
0.300	$l \times 0.171$	1.200	$l \times 0.599$
0.400	$l \times 0.226$	1.300	$l \times 0.634$
0.500	$l \times 0.280$	1.400	$l \times 0.667$
0.600	$l \times 0.332$	1.500	$l \times 0.698$
0.700	$l \times 0.382$	1.600	$l \times 0.726$
0.800	$l \times 0.430$	1.700	$l \times 0.752$

Suppose, as in our case, the box were 12 in. long between the diaphragms, then  $l$  is 6 in. The centre of the instrument is marked with zero, and we find from the table that 0.500 must be placed at  $6 \times 0.280$  in. from the centre on both sides of the centre. Similarly, other points of the scale are found by means of the table. The scale on both sides of zero is symmetrical. The distances between the points so found are subdivided into equal parts. This is not absolutely necessary, but it is convenient.

The movable scale (see Fig. 3) is attached to the upper edge of the taper diaphragm, which is used for reducing the amount of light admitted through the rectangular opening. This taper diaphragm is made of sheet metal about 12 in. long and 2 in. wide, out of which is cut a triangular opening about  $10\frac{1}{2}$  in. in length from base to apex, the width of the base being  $\frac{1}{2}$  in. It is essential that the sides of this triangle be absolutely straight lines. The scale attached to this taper diaphragm is constructed as follows:—From the apex we measure 10 in. exactly towards the base; this gives the zero point of the scale. The other points of the scale are marked so as to read directly the densities. At any distance  $x$  from the apex the area of the opening and, with it, the intensity of the light, will be reduced as  $10 : x$ , and the vulgar logarithm of the fraction  $\frac{10}{x}$  is the corresponding density with which the scale is marked. For convenience we append table showing the distances from the apex, at which the figures 0.1, 0.2, 0.3, &c., are to be placed:—

<sup>1</sup> H.N.—B., p. 55. D.N.—E., p. 13A.

TABLE II.—*Movable Scale.*

Value of $\log. \frac{10}{x}.$	Distance from apex.	Value of $\log. \frac{10}{x}.$	Distance from apex.
	Inches.		Inches.
.00	10	0.50	3.16
.05	8.91	0.60	2.51
.10	7.94	0.70	2.00
.20	6.31	0.80	1.58
.30	5.01	0.90	1.28
.40	4.00	1.00	1.00

Intermediate points are obtained by subdivision into equal parts.

An index is fixed to the inside of the box over the centre of the rectangular diaphragm pointing to the number to be read. The Figs. 1 and 2 will help to make this description clearer.

Two examples will show how the instrument is used.

1. When measuring a small density we move the sliding scale to zero, and the disc chamber to such a position that the images of the Bunsen disc are alike. We then insert the plate to be measured, and without altering the position of the disc chamber slide the movable scale until equality is restored. The density will then be indicated by the fixed index on the diaphragm scale.

2. In the case of a high density we place the sliding scale to 0, and by placing a piece of opal glass outside the box, between it and the lamp, we reduce the light on the right-hand side until the disc chamber requires to be moved almost up to the right-hand end of the box in order to secure equality of the images. If necessary, we move the lamp further away. When equality is thus secured, we read the number below the index of the disc chamber on the fixed scale. We then insert the plate to be measured, and move the disc chamber to the left until equality is again restored. If that cannot be done by the movement of the disc chamber alone, it can be obtained by using the movable scale in addition.

Suppose the index stood at 1.100 on the right, and afterwards at 1.55 on the left of zero, then the density would be  $1.100 + 1.55 = 2.65$ .

If the index stood at 1.10 to the right and afterwards at 1.7 to the left, and equality could then only be restored by using the movable scale as well, and its index pointed to .75, then the density would be  $1.10 + 1.7 + 0.75 = 3.55$ . Higher numbers than 3.55 do not occur in ordinary negatives. A

plate, the density of which is 3.55, only transmits  $\frac{1}{3548}$ th part of the light it receives.

The general rule for finding the density is :—Consider the numbers to the right of zero as negative numbers, those to the left as positive. Subtract the first reading from the second; the result is the density. If the movable scale be used as well, the amount it indicates must be added.

It will hardly be necessary to say that a plate of density 1 permits one-tenth of the light to pass, and that a plate of density 2 permits one-hundredth of the light to pass, since 1 is the log. of 10, and 2 that of 100.

With this instrument we have obtained fairly accurate results. Analyses of mixtures of Indian ink and water, indigo solution and water, and of many other substances have been made by it. The following analyses are given to show the capabilities of the instrument :—

1. *Experiment with Indian ink.*—An Indian ink solution was mixed with water in known proportions, and the density of one solution being known, that of the others was calculated. The following table shows the observed and calculated densities. The calculated density is simply proportional to the amount of Indian ink employed :—

TABLE III.—*Experiment with Indian Ink.*<sup>1</sup>

Indian ink employed to 100 c.c. of water.	Density calculated.	Density found.	C.c. of Indian ink found.
c.c.			
5	.240	.240	5.00
10	.480	.500	10.42
15	.720	.750	15.62
20	.960	.950	19.80
25	1.200	1.245	25.90
30	1.440	1.440	30.0
35	1.680	1.665	34.7
40	1.920	1.885	39.3

The greatest error made does not reach 4 per cent. of the total amount, and even better results can be obtained if more than one reading be taken. But this accuracy is quite sufficient for photographic purposes, where, from other causes, still greater errors are liable to arise, as will presently be shown.

Sometimes, when using the instrument for analysing solutions of coloured salts, a peculiar difficulty arises from the different colours of the two images of the Bunsen disc. This is easily overcome by viewing the disc through appropriately coloured glass—red, green and blue glasses being the most

<sup>1</sup> H.N.—B., pp. 94, 95.

useful. The following experiment with indigo solution is representative of one of the most difficult, since dark blue glass was used to view the disc.

TABLE IV.—*Indigo Solution.*<sup>1</sup>

Indigo solution employed.	Indigo found.	Density calculated.	Density found.
c.c.	c.c.		
100	96.0	1.554	1.487
50	50.6	.777	.787
25	24.1	.388	.375
10	10.0	.155	.155

It will be seen, again, that the results are only accurate within 5 per cent. of their value.

With regard to the lamps, they should be powerful petroleum lamps with duplex burners. The flames should be in planes, at right angles to the axis of the instrument. Very erroneous results are obtained if Argand burners are used. The lamps should be placed close to the diaphragms, and it is advisable to provide a small stage outside the diaphragm to hold coloured glasses, when a substance requires investigation in light of a particular colour.

Captain Abney has also devised an instrument for measuring transparencies. His instrument consists of a Rumford shadow photometer as indicator, and of a revolving sector, which can be closed or opened whilst revolving, as a measure of the transparency. Apart from the fact that a Bunsen disc is more sensitive than the shadows, there is a fallacy in the assumption that the amount of light which passes through a revolving sector is proportional to the angle to which the sector is opened. Experiments made for the purpose show that the amount of light passing through a revolving sector is more correctly represented by a formula—

$$I_x = I \frac{\phi}{360} + C.$$

Where  $I_x$  is the light transmitted by the sector,  $I$  the intensity falling upon the sector,  $\phi$  the angle of opening, and  $C$  a constant, which depends upon the relative position of the lamp, the sector and the screen, and is, in fact, due to the semi-shadow on both edges of the sector openings. The error caused by this constant is small with plates of low density, but it rises to over 100 per cent. with plates of high densities, which renders the results utterly untrustworthy.

<sup>1</sup> H.N.—B., pp. 94, 95.

We have thought it necessary to give this lengthy description of our instrument since we consider it a very important one ; it is for photographic experiments as indispensable as the balance is in analysis. The instrument is capable of other applications ; its indications can always be translated into weights by simply multiplying them with a factor. It is, therefore, capable of applications in analysis.

### III.—DEVELOPMENT.

There is a generally-accepted belief among photographers that a great amount of control can be exercised in development over the density and the general gradations of a negative, and in this respect alkaline pyrogallol enjoys a special reputation. On this account we have chosen this developer for the following series of experiments, except where otherwise stated. These experiments conclusively show that the only control the photographer has over development lies in securing a greater or less density of image (the former often only at the expense of fog), and that he has no control whatever over the gradations of the negative.<sup>1</sup>

The plan we have adopted in carrying out these experiments is to subject *pieces of one and the same plate* to the varying conditions, the influence of which, on the density or the gradation, is the subject of our investigation. A precaution we have always taken, except in our earliest experiments, is never to develop a piece of a plate which has been exposed to the light without simultaneously submitting to the same developer a piece of the same plate which has *not* been exposed, and which we term the "fog strip." The object of this precaution is to ascertain exactly how much of the resulting density is due to the action of the light and how much is due to incidental fog, including therein fog inherent in the plate or caused by injudicious development, and also the density due to glass and gelatine.

In the following series of experiments, made to ascertain the influence of time, of development, and composition of the developer on the density, we covered up one-half of a plate and exposed the other half to a standard light, as will be presently more fully explained. After exposure we cut up the plate in such a way that each piece included a portion of the unexposed and a portion of the exposed plate. Each strip was then developed, such modification in time of development or composition of developer being made as formed the subject of the investigation. The resulting densities were then measured after fixing, washing and drying.

<sup>1</sup> "Gradations" here means "the relative amounts of silver deposited in various portions of the negative"; there is considerable control "over the relative transparencies." See letter Hurter—Bothamley, 5th July, 1890, in D.N.—F., pp. 6, 8.

## Time of Development.

<sup>1</sup> Experiment 1.—Plate : “ Wratten Ord.” Exposure (?) .

Developer, 100 c.c. contain  $\begin{cases} 0.085 \text{ g. NH}_3. \\ 0.400 \text{ pyrogallol.} \\ 0.250 \text{ NH}_4\text{Br.} \end{cases}$

## Results.

Time of development	Minutes	2.5	5.0	7.5	10.0	12.5	15.0
Densities produced	.. ..	1.183	1.543	1.793	1.160	1.10	1.17
Percentage	.. ..	15.6	46.0	67.8	99.1	94.0	100.0

<sup>2</sup> Experiment 2.—Plate : “ Wratten Ord.” Exposure = 60 C.M.S.

Developer, 100 c.c. contain  $\begin{cases} 0.162 \text{ NH}_3. \\ 0.342 \text{ Pyro.}^* \\ 0.228 \text{ NH}_4\text{Br.} \end{cases}$

Time of development	Minutes	1.25	2.5	5	10	15
Density exposed plate	.. ..	1.775	1.175	1.725	2.275	2.475
Density unexposed plate	.. ..	1.155	1.270	1.510	1.590	1.790
Density due to light	.. ..	1.620	1.905	1.215	1.685	1.685
Percentage developed	.. ..	36.8	53.7	72.1	100	100

\* Sulpho-pyrogallol equivalent to pyro.

<sup>2</sup> Experiment 3.—Plate : “ Wratten Ord.” Exposure = 20 C.M.S.

See Diagram No. 1. Developer, 100 c.c. contain :—

0.162 NH<sub>3</sub>.

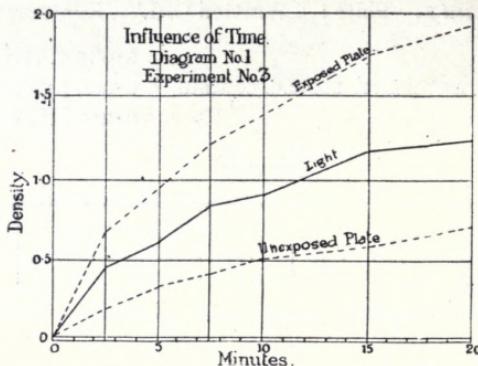
0.342 Pyro.

0.228 NH<sub>4</sub>Br.

Time of development	Minutes	2.5	5	7.5	10	15	20
Density exposed plate	..	1.670	1.965	1.245	1.420	1.755	1.945
Density unexposed plate	..	1.200	1.345	1.415	1.505	1.575	1.710
Density due to light	..	1.470	1.620	1.830	1.915	1.180	1.235
Percentage developed	..	38.0	50.2	67.2	74.1	95.5	100

<sup>1</sup> H.N.—A., pp. 37, 39, 98. H.N.—B., p. 7.<sup>2</sup> D.N.—O., pp. 28, 29; 26.

These experiments show that the total density grows with the time of development, but that the density due to light reaches a limit in about 15



minutes. The continued growth of the total density is due to the action of the developer upon the bromide of silver which had not been affected by the light.

#### *Variation of Pyrogallop.*

<sup>1</sup> *Experiment 4.*—Plate: “Wratten Ord.” Exposure (?).

Developed each strip four minutes in a developer containing in 100 c.c. =

$$\begin{cases} 0.1156 \text{ NH}_3 \\ 0.2000 \text{ NH}_4\text{Br.} \end{cases}$$

Pyrogallop	..	..	..	grms.	0.08	0.16	0.32	0.64
Relative amount	..	..	..	..	1	2	4	8
Density	..	..	..	..	1.036	1.506	1.526	1.500

*Experiment 5.*—Plate: “Wratten Ord.” Exposure = 60 C.M.S. See diagram No. 2.

Developed four minutes in a developer, 100 c.c. =

$$0.162 \text{ NH}_3.$$

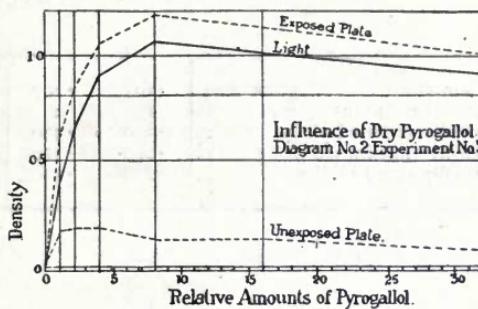
$$0.228 \text{ NH}_4\text{Br.}$$

Pyrogallop used	grms.	.057	0.114	0.228	0.457	0.914	1.828
Relative amount	..	1	2	4	8	16	32
Density exposed plate	..	.595	.840	1.060	1.215	1.150	1.040
Density unexposed plate	..	.180	.195	.190	.130	.135	.105
Density due to light	..	.415	.645	.870	1.085	1.015	.935

<sup>1</sup> H.N.—A., p. 98. H.N.—J., p. 4.

From these results we gather that an excess of pyrogallol beyond a certain limit tends to retard development and the production of density. This limit appears to be the equivalent of pyrogallol necessary to convert the ammonia into tribasic pyrogallate,  $C_6H_3(OH)_4_3$ .

A similar experiment is here given, made with "sulpho-pyrogallol" compounded with sodium sulphite and citric acid. It will be evident that the presence of the acid, by neutralising the ammonia, is responsible for the much more marked falling off in density.



<sup>1</sup> *Experiment 6.*—Plate : "Manchester Slow." Exposure = 40 C.M.S.

Developed 4 minutes, 100 c.c. =  $\begin{cases} 0.162 \text{ NH}_3 \\ 0.228 \text{ NH}_4\text{Br} \end{cases}$ , and "sulpho-pyrogallol" corresponding to  $x$  grms. pyrogallol.

Pyro	..	grms. $x$ =	0.114	0.228	0.457	0.914	1.371	1.828
Relative amount	..	..	1	2	4	8	12	16
Density exposed plate	..	..	.940	1.710	1.610	1.350	.700	.105
Density unexposed plate	..	..	.360	.660	.495	.240	.110	.080
Density due to light	..	..	.580	1.050	1.115	1.110	.590	.025

#### Variation of Ammonia.

<sup>2</sup> *Experiment 7.*—Plate : "Wratten Ord." Exposure (?).

Developed 4 minutes in developer, 100 c.c. =

$x$  grms.  $\text{NH}_3$ .

0.40 Pyro.

0.20  $\text{NH}_4\text{Br}$ .

Ammonia	..	grms.	0.0231	.0462	.0925	.185	.277	.370
Density	..	..	0.00	.613	1.276	1.816	2.136	2.266

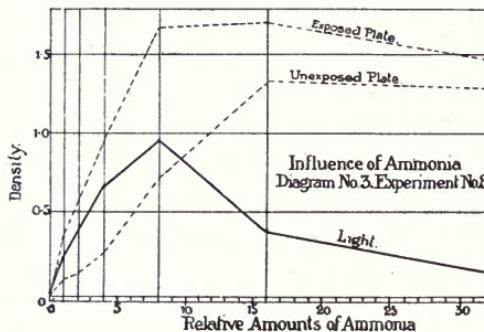
<sup>1</sup> D.N.—O., pp. 25, 33, 24.

<sup>2</sup> H.N.—A., p. 99.

<sup>1</sup> Experiment 8.—Plate : "Wratten Ord." Exposure 20 C.M.S. See diagram No. 3.

$$\text{Developed 4 minutes in 100 c.c.} = \begin{cases} x \text{ NH}_3 \\ 0.34 \text{ Pyro.} \\ 0.23 \text{ NH}_4\text{Br.} \end{cases}$$

Ammonia ..	grms. $x =$	.103	.207	.414	.828	1.656	3.312
Relative amount ..	..	1	2	4	8	16	32
Density exposed plate ..	..	.340	.530	.960	1.675	1.710	1.470
Density unexposed plate ..	..	.090	.120	.265	.700	1.310	1.300
Density due to light ..	..	.250	.410	.695	.975	.400	.170



<sup>1</sup> Experiment 9.—Plate : "Manchester Slow." Exposure 40 C.M.S. See diagram No. 4.

$$\text{Developed 4 minutes in 100 c.c.} = \begin{cases} x \text{ NH}_3 \\ 0.34 \text{ Pyro.} \\ 0.23 \text{ NH}_4\text{Br.} \end{cases}$$

$x$ grms. $\text{NH}_3$ ..	..	.207	.414	.828	1.242	1.656	3.726
Relative amount ..	..	1	2	4	6	8	18
Density exposed plate ..	..	.250	1.530	2.290	2.470	2.470	1.865
Density unexposed plate ..	..	.090	.550	1.400	1.880	2.015	1.445
Density due to light ..	..	.160	.980	.890	.590	.455	.420

The general result of these experiments is that the addition of ammonia, up to a certain extent, increases the density in a given time, but that the amount of ammonia which can be added without giving rise to fog, and without simul-

aneously adding bromide, is very limited. The so-called accelerating action of ammonia being due almost entirely to its solvent action on bromide of silver, which, if the ammonia is increased sufficiently, results in greatly diminishing the density.

The following table shows the solubility of silver bromide<sup>1</sup> in very dilute ammonia, such as is used for development of plates :—

100 c.c. of dilute ammonia containing—

1.105 grms. NH <sub>3</sub>	dissolve	0.0376 AgBr.
·555	"	0.0206 "
·162	"	0.0100 "
·0897	"	0.0052 "

The last two solutions represent the extreme concentrations usually employed by photographers for development.

If to any of these solutions of silver bromide in ammonia, bromide of ammonium be added, an immediate precipitate of bromide of silver is the result. The so-called accelerating action of ammonia, and the retarding action of ammonium bromide, are probably due entirely to this solvent action of the one and the anti-solvent action of the other of these two reagents. The rapid production of fog when ammonia is increased is due to the fact that when pyrogallol solution is added to an ammoniacal solution of bromide of silver, the silver in solution is precipitated immediately in the metallic state.

The following experiments show the influence of—

#### *Variation of Ammonium Bromide.*

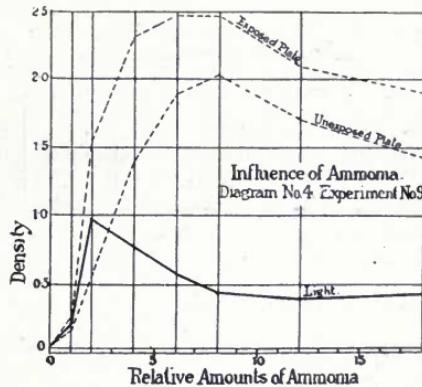
<sup>2</sup> *Experiment 10.*—Plate : “Wratten Ord.” Exposure (?).

Developed for 4 minutes, 100 c.c. =  $\begin{cases} 0.123 \text{ NH}_3 \\ 0.375 \text{ Pyro.} \end{cases}$

Ammonium bromide, grms. in 100 c.c.	..	..	..	0.00	0.10	0.20	0.40	0.80	1.28
Relative amount	..	..	..	0	1	2	4	8	12.8
Density	..	..	..	1.81	1.73	1.61	1.43	0.34	0.00

<sup>1</sup> D.N.—A., p. 124.

<sup>2</sup> H.N.—A., p. 98. H.N.—J., p. 3.

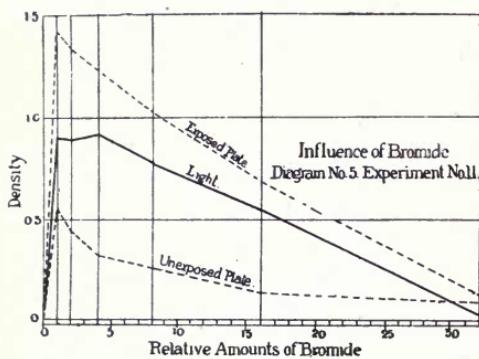


<sup>1</sup> Experiment II.—Plate : "Wratten Ord." Exposure = 40 C.M.S.

Developed 4 minutes in 100 c.c. =  $\left\{ \begin{array}{l} 0.162 \text{ NH}_3 \\ 0.342 \text{ Pyro.} \end{array} \right.$  and various amounts of bromide. See Diagram No. 5.

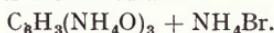
Ammonium bromide .. ..	.057	.114	.228	.457	.918	1.828
Relative amount .. ..	1	2	4	8	16	32
Density exposed plate .. ..	1.450	1.335	1.235	1.025	.685	.120
Density unexposed plate .. ..	.560	.455	.315	.255	.130	.090
Density due to light .. ..	.890	.880	.920	.770	.555	.030

It is clear that development in both experiments was entirely prevented in these four minutes when the amount of bromide was about ten times that of ammonia present.



Influence of Bromide  
Diagram No. 5 Experiment No. II

It also appears from our experiments that a rational developer would consist of a decinormal solution of ammonia, containing so much pyrogallol and ammonium bromide as would correspond with the formula—



We have represented many of these results in the form of diagrams. It will be interesting just to point to Diagrams Nos.

1, 3 and 4, to show the great amount of action which the alkaline developer may have on the bromide of silver, although it has never been exposed.

This disagreeable property is common to all alkaline developers, and it renders them unsuitable for scientific investigations. In all our important work we use exclusively the ferrous oxalate developer, for the reason that it attacks unexposed bromide of silver so slowly, that within one hour and even more no appreciable density can be developed upon a really good plate. Nor does its action vary much with its composition. The addition or omission of bromide from the constitution of this developer does not seem to have any great influence, and a greater or less concentration of the reagents within considerable limits does not affect its action; indeed, we have not found any variation to arise from alterations in its composition, excepting the length of time needed for completion of development.

The following table shows how the density of an exposed plate grows as the time of development is prolonged from five minutes to one hour :—

<sup>1</sup> *Experiment 12.—Ferrous Oxalate.*

Time.	Density exclusive of fog.				
	I.	II.	III.	IV.	V.
Minutes.					
5	.365	.350	—	—	.215
10	.525	.460	—	—	.305
15	.615	.550	.795	.570	.410
20	.615	.575	—	—	.420
25	.700	.650	—	—	—
30	.700	.660	.860	.670	.450
45	—	—	1.000	.715	.515
60	—	—	—	.740	—

Columns I and II are the results obtained upon the same plate, one (I) portion of the strips developed in a developer consisting of four parts of a saturated solution of potassium oxalate, mixed with one part of a saturated solution of ferrous sulphate, the other (II) portion of the strips developed in the same developer diluted with an equal volume of water. Columns III and IV represent other experiments, the plates being developed with the saturated solution. Whilst I to IV were developed with a small amount of bromide of potassium added to the developer, No. V was developed without bromide. In not one instance did the density of the unexposed portions of the plate amount to more than 0.098, which is the density due to clear glass and gelatin. That ferrous oxalate does not, however used, attack silver bromide which has not been exposed to light is a most valuable and characteristic property of this developer.

An important result of this series of experiments is that the density reached is dependent upon the time of development as well as upon the exposure of the plate. The time it takes to reach a given density varies much with the gelatin employed in making the emulsion and the age of the plate. But with each plate it obeys a certain law, which is more or less clearly visible in every one of the five experiments. The density grows rapidly at first, its growth becoming slower as time advances, and finally tends to a limit. Each experiment is, taken by itself, liable to many errors; but by reducing every experiment to the densities obtained in No. IV, in simple proportion, the following tabulated series of numbers is obtained :—The columns marked I,

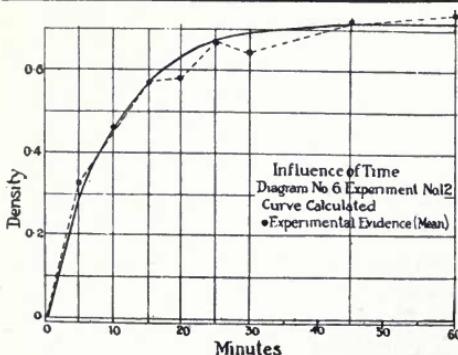
<sup>1</sup> D.N.—F., p. 21.

II, &c., are the reduced densities of the corresponding columns of Experiment 12. The column marked "Mean" shows the arithmetical mean for any period of development obtained from the five series. The column "Calculated" is obtained by means of a formula based upon the idea that the number of particles of bromide of silver affected by the light is greatest in the front layer of the film and decreases in geometrical progression as each succeeding layer of the film is reached, an idea which will be better appreciated when we have explained the action of the light upon the film. This idea expressed algebraically leads to the formula—

$$D_t = D (1 - a^t),$$

where  $D_t$  is the density after  $t$  minutes development,  $D$  the limit of density reached by very prolonged development, and  $t$  the time of development,  $a$  is a fraction depending upon the nature of the film, concentration of developer, temperature, &c. The constants for the series of figures below are  $D = 0.720$ ,  $a = 0.9015$ .<sup>1</sup>

Time.	Recalculated — Densities.						
	I.	II.	III.	IV.	V.	Mean.	Calculated.
Min.							
5	.349	.350	—	—	.298	.332	.290
10	.502	.460	—	—	.423	.462	.464
15	.588	.550	.569	.570	.569	.569	.568
20	.588	.575	—	—	.583	.582	.628
25	.670	.650	—	—	—	.660	.665
30	.670	.660	.615	.670	.625	.645	.687
45	—	—	.715	.715	.715	.715	.713
60	—	—	—	.740	—	.740	.719



The relation of the calculated figures to the experimental data is best seen in Diagram No. 6.

A very important conclusion can be shown to proceed from the formula representing the course of development.

If on any one plate two exposures are given, one of which would ultimately yield density  $D_1$  and the other  $D_2$ , and if this plate

were developed for a time  $t$ , then two densities,  $d_1$  and  $d_2$ , would result such that :-

$$d_1 = D_1 (1 - a^t)$$

$$d_2 = D_2 (1 - a^t)$$

and it will be seen that, on dividing these equations—

$$\frac{d_1}{d_2} = \frac{D_1}{D_2}$$

the resulting ratio is independent of the time of development, and is equal to the ratio of the ultimate densities which would be reached, so that the gradation<sup>1</sup> of negatives appears to be independent of the time of development.

#### IV.—GRADATION.

The above experiments have shown that with a well-balanced developer there is a limit to density, which depends upon the action of the light, and that, so far, the only control the photographer has lies in deciding whether he will reach that limit or not.

It also became evident that if two different densities be developed upon the same plate to their extreme limits, the ratio existing between these limits must depend solely upon the action of the light. The question we have now to consider is whether it is possible by any modification of development to influence this ratio, and whether this same ratio exists at all stages of development.

In making these experiments the source of light we have adopted is a standard candle placed at 1 metre distance from the plate. We then produce a number of gradations upon the plate by exposing different portions of it to the light for different periods of time, always leaving one portion of the plate unexposed.

In order to show that the length of time of development does not affect the ratio of densities among themselves, but increases every density by proportional amounts, we give the following experiments, made with various plates, ferrous oxalate being the developer used. The table show the densities obtained, their ratio among themselves, and the ratios of the two corresponding densities obtained by long and short development.

All densities are given exclusive of fog (the density of unexposed plate being subtracted from density of exposed plate).

<sup>1</sup> "Gradation" here means the ratio of the densities.

## Experiment 13.—Gradations. Ferrous Oxalate.

Plate used.	Exposure, C.M.S.	Short development, 4 minutes.		Long development, 12 minutes.		Ratio $\frac{D_2}{D_1}$	Remarks.
		Density $D_1$ .	Ratio.	Density $D_2$ .	Ratio.		
Ilford Red Label. (1.)	10	.775	1.0	1.260	1.0	1.63	Greatest error, $\pm$ 2.4 per cent.
	20	1.000	1.29	1.660	1.31	1.66	
	40	1.180	1.52	1.96	1.55	1.66	
	80	1.250	1.61	2.08	1.65	1.60	
				Mean ...	...	1.64	
Wratten's Drop Shutter. (2.)	10	1.17	1.0	1.74	1.0	1.50	Greatest error, $\pm$ 3.4 per cent.
	20	1.67	1.42	2.37	1.36	1.42	
	40	2.06	1.76	2.91	1.67	1.41	
	80	2.26	1.93	3.33	1.91 <sup>a</sup>	1.47	
				Mean ...	...	1.45	
" United Kingdom." (3.)	10	.160	1.0	.275	1.0	1.70	Greatest error, $\pm$ 5 per cent.
	20	.313	1.95	.485	1.76	1.55	
	40	.518	3.23	.830	3.01	1.60	
	80	.703	4.39	1.145	4.14	1.63	
				Mean ...	...	1.62	
1							

The greatest errors are comprised within those limits within which our method of measuring densities is only reliable.

The results clearly show that the ratio of densities is given by the light alone, and is not affected by the time of development, a fact quite in accordance with the conclusions previously arrived at.

This ratio, we find, is altogether unalterable. No modifications we have made in developers or in development has ever seriously disturbed this ratio of the densities. We quote the following few experiments in support of this statement.

<sup>2</sup> *Experiment 14.*—The plate, a "Manchester Slow," having received three different exposures, was cut into four portions; two were developed with

<sup>1</sup> D.N.—O., p. 2. H.N.—I., p. 1. <sup>2</sup> D.N.—O., p. 21. H.N.—I., pp. 1 and 2.

hydroquinone and two with eikonogen for different lengths of time. The densities are given exclusive of fog, which, with both developers, was very considerable :—

Developer.	Exposure, C.M.S.	Short develop.		Long develop.		Ratio $\frac{D_2}{D_1}$	Remarks.
		Density $D_1$ .	Ratio.	Density $D_2$ .	Ratio.		
Hydro-quinone.	10	.485	1.0	.785	1.0	1.61	Short time = 2.5 m. Long time = 7.5 m. Mean ratio, 1.55. Greatest error, 4 per cent.
	20	.875	1.80	1.385	1.76	1.58	
	40	1.450	3.0	2.120	2.70	1.47	
Eikonogen.	10	.310	1.0	.580	1.0	1.87	Short time = 4 m. Long time = 12 m. Mean ratio, 1.79. Greatest error, 4.4 per cent.
	20	.560	1.81	.980	1.7	1.75	
	40	.905	2.92	1.600	2.76	1.76	

<sup>1</sup> Experiment 15 shows that the same result is obtained with pyrogallol development. Plate used : "Manchester Slow." Densities exclusive of fog :—

Exposure, C.M.S.	Developed, 3 minutes. Ammonia added at once.		Developed, 18 minutes. Ammonia added in six doses every 3 minutes.		Ratio $\frac{D_2}{D_1}$	Remarks.
	Density $D_1$ .	Ratio.	Density $D_2$ .	Ratio.		
10	.385	1.0	.420	1.0	1.09	Mean ratio, 1.15. Greatest error, 5 per cent.
20	.770	2.0	.850	2.0	1.10	
40	1.095	2.84	1.315	3.1	1.19	
80	1.455	3.7	1.765	4.0	1.21	

<sup>2</sup> Experiment 16 is important because it contradicts emphatically the belief that gradations of an over-exposed negative can be altered by using greater amounts of bromide. Plate : "Manchester Slow."

<sup>1</sup> D.N.—O., p. 20. H.N.—I., p. 2.

<sup>2</sup> D.N.—O., p. 23.

Exposure, C.M.S.	Developed, 4 minutes. 100 c.c. = 0.22 NH <sub>4</sub> Br.		Developed, 12 minutes. 100 c.c. = 0.66 g. NH <sub>4</sub> Br.		Ratio $\frac{D_2}{D_1}$	Remarks.
	Density $D_1$	Ratio.	Density $D_2$	Ratio.		
10	.440	1.0	.485	1.0	1.10	Mean ratio, 1.15.
20	.840	1.91	.965	1.98	1.15	Greatest error, 4.3 per cent.
40	1.200	2.73	1.440	2.97	1.20	
80	1.625	3.70	1.900	3.90	1.16	

*Experiment 17.*—For this experiment a "Wratten Ordinary" plate received four different exposures. It was then cut into four portions, and each portion was developed with a different developer. The result is extremely interesting and important, since it shows that the ratio between the various densities is identically the same whatever developer is employed, except in the case of eikonogen, in which the ratios are a little different. We shall recur to this difference in another place.

#### TIME OF DEVELOPMENT DIFFERENT FOR EACH DEVELOPER.<sup>1</sup>

Ex- posure.	Ferrous oxalate.		Pyrogallol.		Hydroquinone.		Eikonogen.	
	Density.	Ratio.	Density.	Ratio.	Density.	Ratio.	Density.	Ratio.
C.M.S.								
10	.310	1.0	.320	1.0	.410	1.0	.300	1.0
20	.535	1.7	.550	1.7	.695	1.7	.470	1.6
40	.810	2.6	.805	2.5	1.000	2.4	.645	2.2
80	1.080	3.5	1.005	3.1	1.400	3.4	.820	2.7

These experiments all confirm the statement that the gradations of a negative, as expressed by the ratios of the densities, are independent of time of development, cannot be affected by alterations in the composition of the developers, and are almost identically the same whatever developer is employed. We are thus driven to the conclusion that the photographer has no control over the gradations of the negative, the ratios of the amount of silver deposited on the film being solely dependent upon the exposure. The photo-

<sup>1</sup> D.N.—O., p. 14; H.N.—K., p. 25.

grapher has the power to increase the total density by prolonged development, but by no means at his disposal can he alter the ratios existing between the amounts of silver reduced in the various parts of the negative. They are regulated entirely by the exposure.

These ratios are not even altered by intensification after development, as is shown by the following results :—

#### INTENSIFICATION.

<sup>1</sup> *Experiment 18.*—Plate “Wratten Ordinary,” exposed and developed with ferrous oxalate, measured and afterwards intensified and measured again :—

Exposure.	Before intensification.		After intensification.		$\frac{D_2}{D_1}$
	Density $D_1$ .	Ratio.	Density $D_2$ .	Ratio.	
10	.31	1.0	.60	1.0	1.93
14	.50	1.61	.91	1.5	1.82
20.5	.67	2.16	1.30	2.16	1.94
29.3	.86	2.77	1.71	2.85	1.98
41.9	1.03	3.32	2.15	3.5	2.08
60	1.30	4.19	2.56	4.2	1.96
				Mean ...	1.95

It will be seen that the process of intensification has almost exactly doubled the amount of silver<sup>2</sup> on the plate. Almost the same result was found in the following experiment :—

<sup>3</sup> *Experiment 19.*—Similar to last experiment.

Exposure.	Before intensification.		After intensification.		Ratio $\frac{D_2}{D_1}$
	Density $D_1$ .	Ratio.	Density $D_2$ .	Ratio.	
10	.260	1.0	.475	1.0	1.82
20	.460	1.8	.850	1.8	1.85
40	.700	2.7	1.270	2.6	1.81
80	.950	3.6	1.700	3.6	1.79
				Mean ..	1.82

<sup>1</sup> H.N.—A., p. 143. H.N.—B., p. 8.

<sup>2</sup> This should be “density,” not “silver.” See Corr. Hurter—Chapman Jones, October, 1890.

<sup>3</sup> D.N.—O., p. 22.

In this case intensification did not quite, but very nearly, double the amount of *silver*<sup>1</sup> in each density, but the ratio existing between the several gradations is, again, not affected at all.

We see, therefore, that whatever may have been the mode of development employed, and whether intensified or not, the ratios of densities are characteristic of the action of the light, and can be alone relied on in investigations respecting the action of the light on the sensitive film.

#### REDUCTION.

There is only one process known to us, so far, which will totally alter the ratios existing between the deposits of silver on a negative, viz., the process of reduction, that process consisting in immersing the developed plate into a solution of potassium ferricyanide and sodium thiosulphate (hyposulphite). This process so alters the ratios that photographers ought to use it very cautiously.

<sup>2</sup> *Experiment 20.*—Plate exposed, measured, and reduced by immersion in potassium ferricyanide and sodium thiosulphate :—

Exposure.	Before reduction.		After reduction.		Ratio $D_1$ . $D_2$ .
	Density $D_1$ .	Ratio.	Density $D_2$ .	Ratio.	
10	.410	1.0	.020	1.0	20.5
20	.655	1.6	.130	6.5	5.0
40	1.010	2.46	.365	18.2	2.7
80	1.450	3.5	.680	34.0	2.1

#### V.—ACTION OF LIGHT ON SENSITIVE FILM.

Our investigations have not only revealed the fact that one single density taken by itself is not characteristic of the exposure which the sensitive film received, since the density may be partially due to "fog," or may not be developed to its extreme limit, but the experiments have also clearly shown that the ratio of two densities, exclusive of fog, is a function of the action of the light on the plate. It will be noticed that in all these experiments the exposures given varied between 10 seconds and 80 seconds, and the source of light was always a standard candle placed exactly one metre off the plate. If we tabulate the ratios found between the 10 seconds and 80 seconds

<sup>1</sup> Should be "density." Corr. Hurter—Chapman Jones, Oct., 1890. <sup>2</sup> D.N.—G., p. 22.

exposures in these experiments, we see at once that the ratio, though constant for one particular plate, is very different for different plates.

Name of plate.	Ratios of densities for		Experiment No.
	Exposures $\frac{40''}{10''} = 4$	Exposures $\frac{80''}{10''} = 8$	
Ilford " Red Label " ..	1.53	1.63	13
Wratten " Dropshutter " ..	1.71	1.92	13
" United Kingdom " ..	3.12	4.27	13
" Manchester Slow " ..	2.97	3.82	15
Do. ..	2.85	3.80	16
Do. ..	2.84	—	14
Own make ...	Batch A ..	Exposures $\frac{160''}{20''} ..$	8.00
	.. A ..	$\frac{240''}{30''} ..$	5.30
	.. A ..	$\frac{1440''}{180''} ..$	3.00

The ratio is for the same exposures, smaller for rapid plates than for slow plates, but even with the same plate the ratio between two densities varies for exposures which bear the same ratio to each other, but are different in absolute value, as is seen from the experiments given in the above table, and made with plates prepared by ourselves.

It is certain, therefore, that the ratio between two densities depends not only on the ratio of the exposures, but also on the sensitiveness of the plate and the absolute values of the exposures. The following investigations were made to discover the connection existing between exposure, sensitiveness and density produced :—

*Unit of Exposure.*—For these investigations it was necessary to adopt a standard unit of exposure. As unit of light we have chosen the intensity of a standard candle at one metre distance, and as unit of time the second, so that our unit of exposure is the product of the intensity of the standard candle at one metre distance and the second, and we call this unit of exposure one "candlemetre-second." We find for experimental purposes, with plates of average speed, it is an excellent unit, easily procured, and of sufficient constancy to permit of satisfactory repetitions of experiments. There are a few precautions necessary to ensure uniform results. The flame of the candle cannot be relied on until it has settled to a height of nearly 45 mm., measured from the top of the spermaceti to the top of the flame, as shown in Fig. 4. The candle must be protected against draughts, and this is best done by placing

it within a black box having one side open. This also prevents the illumination of bright objects on the working table and consequent reflections. The candle should be extinguished by an extinguisher and kept covered up while not in use.

As regards measuring time of exposures, we use a chronograph watch, or a metronome for short exposures, but we find that errors of exposure become too great if less than 10 seconds are measured. If we wish to give shorter exposures than 10 candlemetre-seconds (C.M.S.) we place the standard candle two metres off, thus reducing its intensity to one-quarter.

It is scarcely necessary to say that we have carefully ascertained that within such limits of exposures as our experiments embrace it is immaterial whether an exposure be made with a light of one-quarter candlemetre for 40 seconds or a light of one candlemetre for 10 seconds. We have also proved by experiment that, as far as the ratios of densities are concerned, they remain constant, whether the exposure be made with a candle, with a petroleum lamp, or with daylight, so long as the product of intensity of light and time of exposure be the same. The intensities of such different sources of light cannot, however, for this purpose be compared by the ordinary Bunsen photometer, but must be compared by photographic experiments. But with careful work even single densities can be reproduced with tolerable accuracy. For instance, on three separate days we obtained on three separate plates of the same batch by carefully measuring the time, both of exposure and of development, densities 0.750, 0.730 and 0.720 respectively. Four different standard candles gave upon one plate in 10 seconds the following densities:—0.490, 0.490, 0.500, 0.480.

With the standard candle we investigated, in the first place, the general effect of prolonged exposure on the density, *i.e.*, we ascertained how much silver was reduced by different exposures.

<sup>1</sup> *Experiment 21.*—A “Manchester Slow” plate exposed, developed with ferrous oxalate, and measured, gave:—

Exposure, C.M.S.	Density.	Difference.	Exposure, C.M.S.	Density.	Difference.
0.625	.045	—	80	1.010	.255
1.25	.055	0.010	160	1.270	.260
2.50	.085	0.030	320	1.555	.285
5.00	.175	0.090	640	1.885	.330
10.0	.250	.075	1,280	2.088	.203
20	.400	.210	2,560	2.262	.174
40	.755	.295	5,120	2.352	.090

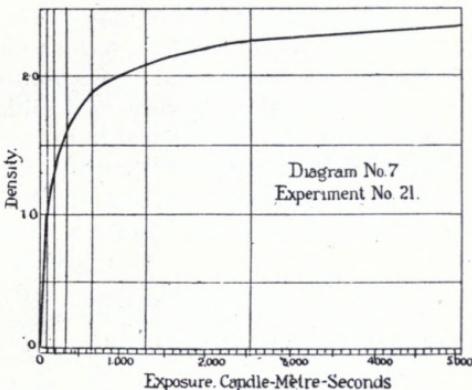
<sup>1</sup> D.N.—O., pp. 7, 8. Corr. Driffield—Chapman Jones, 17th July, 1890.

It will be seen that, every time the exposure is doubled, the density increases, at first slowly, then considerably, and (disregarding errors of experiment) from 40 C.M.S. up to 1,280 C.M.S. every time the exposure is doubled, nearly an equal addition to density is the result, the addition to the density being on an average 0.266, but after an exposure of 1,280 C.M.S. further doubling produces less and less increase in density. The first few densities are too small to admit of accurate measuring.

This series of results is represented graphically on diagram No. 7, the exposures being chosen as abscissæ, the densities as ordinates; from this diagram it will be seen at once how rapidly densities grow at first as exposure is increased, and how slowly at last the densities tend towards a limit.

The following series of exposures is carried still further in order to ascertain the character of the curve representing the action of the light on the silver bromide, and to learn, if possible, something of the limit towards which the curve tends.

<sup>1</sup> *Experiment 22* :—



Exposures, C.M.S.	Densities.	Difference.	Exposures, C.M.S.	Densities.	Difference.
1	.060	—	1,024	2.985	+ 450
2	.160	+ 100	2,048	3.115	+ 130
4	.340	+ 180	4,096	3.280	+ 165
8	.500	+ 160	8,192	3.405	+ 125
16	.715	+ 215	16,384	3.508	+ 103
32	.940	+ 225	32,768	3.474	— 0.034
64	1.345	+ 405	65,536	3.280	— 0.194
128	1.875	+ 530	131,072	3.128	— 0.162
256	2.290	+ 415	262,144	2.920	— 0.208
512	2.535	+ 245	524,288	2.464	— 0.456

This series of results could not be graphically represented to advantage by choosing exposures as abscissæ since they vary from one candlemetre-

<sup>1</sup> H.N.—B., p. 136.

second to over half a million. But it is evident that prolonged exposure gradually reduces the density attainable after development.

The graphic representation of Experiment 22 on the same scale as Experiment 21 would require a diagram about 500 times as long as Diagram No. 7, and nothing of any value would be learnt from such a diagram.

What we really wish to ascertain is whether it is possible to produce a theoretically perfect negative, such as was defined, and what the connection is between the densities and the exposures.

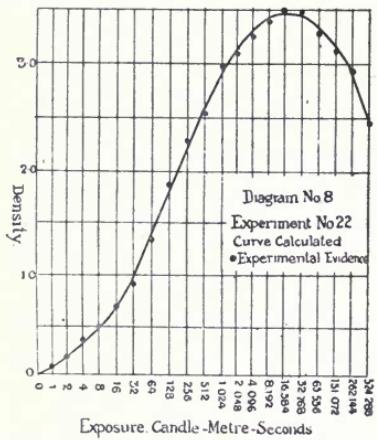
If in any part of the curve of densities, as represented in Diagram No. 7, the densities were proportional to the logarithm of the exposures, we should discover that portion of the curve if, instead of choosing the exposures as abscissæ, we used the logarithms of the exposures as abscissæ. This is easily done when the exposures progress, as they always do in our experiments,

in a geometric series. We have only to mark every new exposure equi-distant from the previous one as abscissæ. In this manner the results of Experiment 22 are plotted in Diagram No. 8.

It will be perceived that the curve now consists of four distinct branches. It proceeds from exposure 1 in almost horizontal direction, ascends slowly to exposure 16, from thence it proceeds almost in a straight line to exposure 2,048, when the growth of densities becomes slow. The densities reach their maximum at exposure 16,384, and from thence the curve returns, the densities diminishing slowly with increased exposures.

We accordingly distinguish four different periods of exposures. The first period we term the period of "under-exposure"; it is comprised in the first curved portion. The second period, that during which the curve is almost a straight line, we call the "period of correct representation." The third period is that during which the curve is again strongly bent as far as its maximum. This is the period of "over-exposure," and the last portion of the curve we term the period of "reversal."

*1. Period of Under-exposure.*—During this period the ratios between two densities are at first accurately equal to the ratio of the corresponding



exposures. It is very difficult to study this portion of the curve accurately, owing to the short exposures which it demands, but still more owing to the small densities which this period yields, and which are difficult to measure. By making very slow emulsions we have, however, succeeded in showing clearly that at first the amount of silver reduced is proportional simply to the exposure. Thus, a plate made by ourselves, with pure bromide of silver, gave the following results :—

Exposure, 20 C.M.S.	Density, .125 or 1.
, 160     ,     ,	1.055 or 8.4.

The ratio between the densities being very nearly 8, the ratio of exposures.

Again, a "United Kingdom" plate gave the following results :—

Exposure, 2.5 C.M.S.	0.160.	Ratio, 1.
, 5.0     ,     ,	0.313.     ,     , 1.95.	

A very slow "Manchester" plate gave the following results :—

1 C.M.S.	0.260.	Ratio, 1.
2     ,     ,     ,     ,     ,     , 2.1.	0.550.     ,     ,     ,     ,     ,     ,	

But of course there is no definite point which marks the end of this period and the beginning of the next. But it is from this period that we learn that, for short exposures, *the amount of silver reduced is directly proportional to the exposure.*

*Period of Correct Representation.*—The second period of exposures we have thus named because during this period a plate is capable of giving a negative differing as little as possible from that which, at the beginning, we defined as theoretically perfect. That definition demanded that the densities of the negative should be proportional to the logarithms of the exposures which produced them. It is characteristic of this period that *the densities are proportional to the logarithms of the exposures.* This is shown on Diagram No. 8, where the densities are the ordinates, the logarithms of exposures are abscissæ, and the period of correct representation a straight line. We have measured densities of dozens of plates falling within this period, and we find them all to conform to this very simple linear equation—

$$D = \gamma [\log. I.t \pm C],$$

D being the density,  $\gamma$  a constant depending on time of development, I.t the product of intensity of light and time, *i.e.*, the "exposure," and C a constant depending upon the speed of the plate. As we shall give further detailed proof of this, we will here merely insert one example of a plate the constant

C of which is zero. It is Plate 2 of Experiment No. 13. That plate gives the following results with equation :—

$$D = 1.75 \times \log. \text{exposure.}$$

Exposure.	Density found by experiment.	Density calculated.
10	1.74	1.75
20	2.37	2.27
40	2.91	2.75
80	3.33	3.30

Many similar examples will be quoted presently.

We have thus arrived at the answer to the question, Can negatives be produced such as we defined to be theoretically perfect? And this answer is, They *can* be produced, but only by so carefully adjusting the time to the intensity of the light that the exposures may fall within that period of correct representation. No variations whatever in development will correct an under or over-exposure.

*Period of Over-exposure.*—Little need be said about this period. As the curve tends to become parallel to the axis of abscissæ it is clear that when exposures fall within this period, shadows and high lights will all be represented by densities which are almost equal. There will be no contrasts. In the first period of under-exposure the contrasts are too great. Here they are too small.

*Period of Reversal.*—This period we have named the period of reversal because within this period happens that peculiar phenomenon, the transformation of the negative into the positive, the "solarisation," "reversal," &c. It is easy to understand how the negative becomes a positive. Whilst the deep shadows still act upon the plate, increasing the density, the high lights have passed their maximum and their densities grow less and less. The more the exposure is prolonged the less dense the high lights become, the shadows exceeding them in density. It is quite easy to observe this phenomenon of reversal with a powerful petroleum lamp or gas burner, or to produce by direct contact printing a secondary negative, instead of a positive, from the original negative, by about 15 to 20 minutes' exposure at 6 in. distance from the light. When, in the camera, exposure is prolonged, it is well known that a positive is obtained instead of a negative. It has been stated by Jansen that a secondary negative and a secondary positive can be obtained by prolonging the exposure still further. We have not, however, been able to verify this statement, and we believe it to be erroneous. Our investigations show

that the density tends to a limit, and a picture produced by prolonged exposure in the camera is gradually lost in a uniform veil of fog, though it is still visible even after three days' exposure.

A "United Kingdom" plate received various prolonged exposures, with the following results:—

						Difference.
75,000	C.M.S.	gave density	..	..	1.415	
150,000	„	„	..	..	1.111	.304
300,000	„	„	..	..	.970	.141
600,000	„	„	..	..	.925	.045

A piece of the same plate exposed to direct daylight for 90 minutes (about six million C.M.S.) gave a density 1.200. From this it appears to us that there is an equilibrium established between the action of the refrangible and less refrangible rays.

The period of reversal is, theoretically, exceedingly interesting, and deserves further careful study, but the reversing action is so slow, and requires such enormous exposures, that it does not need to be considered from a practical point of view, and we shall disregard it entirely for the present. The three first periods, that of under-exposure, that of correct representation, and that of over-exposure, are the only practically interesting portions of the curve. We have already stated that, during the first period, the ratio of densities is equal to the ratio of exposures, *i.e.*, the amount of bromide of silver reduced is proportional to the exposure, whilst, during the second period, the density only grows in proportion to the logarithm of the exposure. It almost ceases to grow during the third. Of course, these assertions are only two approximate statements of one single law connecting the densities with the exposures.

All photo-chemical investigations which have hitherto been made have proved that the amount of chemical action is proportional to the "exposure" (*i.e.*, the product of intensity of light and time). The sensitive film of the photographic plate forms no exception to this general law, and we take it as a fundamental truth that the amount of action upon the plate is, at any moment of the exposure, proportional to the energy which the plate receives at that moment. During the first period, when the surface, or chiefly the surface of the film, is acted upon, the results of the investigations have shown this to be true accurately. But when the action of the light upon particles of bromide of silver below the surface has to be considered, the question arises, How much of the light which impinges on the surface really reaches those particles?

Of the rays of light which impinge upon the surface of the sensitive plate, some are reflected and some pass right through the plate.<sup>1</sup> If one sensitive plate be exposed to light behind another, it will be found that it also is affected.

The energy of the reflected and transmitted light cannot, obviously, play any part in the molecular work to be done in the film. It is useless photographically.

The light absorbed in the film is the only light which contributes towards the formation of the "latent image," but not even the whole of the light which is absorbed does useful work. It can be proved experimentally that a plate which has received such an exposure as to yield maximum density on development absorbs exactly as much light as a plate which has not been exposed at all, yet the light absorbed by a plate already so exposed obviously contributes nothing towards increase of density.

From this it is clear that the light absorbed by a particle of silver bromide, which has already received sufficient energy to bring it into that condition in which it is capable of development, is useless.

It will therefore be evident that, of the light impinging upon the plate, there is only one portion useful, viz., that which is absorbed by unaltered silver bromide, the light reflected, the light transmitted, and the light absorbed by particles of silver bromide already changed, being altogether useless.

The amount of work done at any moment of the exposure is therefore proportional to the amount of energy received by the unaltered silver bromide only.<sup>2</sup>

It is very easy to state this proposition mathematically, and thus find the law which connects the densities with the exposures.

If the intensity of the light (with respect to chemically active rays) is  $I$ , and the fraction of the light reflected from the surface of the film is  $a$ , then the amount  $(1 - a) I$  enters the film. If the film contains, at the moment we are considering,  $x$  particles of silver bromide per unit area, which are already changed, then the transparency of the plate with respect to the changed particles is  $e^{-kx}$ , i.e., this is the amount of light which passes the particles already changed. If from this amount we deduct the amount of light which passes *all* the particles of silver, changed or unchanged, the difference represents the amount of light absorbed by the silver bromide not yet affected. Now the light which passes all the particles of silver, if there are  $a$  of them per unit area, will be measured by the transparency of the plate, viz.,  $e^{-ka}$ . Deducting this from  $e^{-kx}$  and multiplying the difference with the total amount of light entering the film will give the mathematical expression for

<sup>1</sup> H.N.—B., pp. 43, 53, 59.

<sup>2</sup> H.N.—D., p. 83, and Dr. Allen's paper in this vol., p. 34.

the amount of light which, at the moment we are considering, can do useful work. This amount is:  $(1 - a) I (e^{-kx} - e^{-ka})$ . If this expression is multiplied by the short time of exposure  $dt$ , it will represent the amount of useful energy conveyed to the plate during that time.

Suppose it requires an amount of energy  $e$  to change one particle of silver bromide into the condition capable of development, then the number of particles  $dx$  so changed during the time  $dt$  will be—

$$(1.) dx = \frac{I}{e} (1 - a) [e^{-kx} - e^{-ka}] dt.$$

This is the complete mathematical expression of the idea that it is only that portion of the light which is absorbed by unchanged silver bromide which contributes to the growth of density.<sup>1</sup>

By integration of equation (1), and by substitution of the symbol  $O$  for  $e + ka$ , we find that the density of the "latent image" (before development) is—

$$D = \log_{\epsilon} [O - (O - 1) \beta^{k(1-a) \frac{It}{e}}]$$

where  $\beta$  is a fraction, the hyperbolic logarithm of which is  $-\frac{I}{O}$ ,  $O$  is simply the opacity of the plate to the chemically active rays before exposure.

In this derivation of the connection between the density  $D$  and the exposure  $It$ , two assumptions have been silently made which need explanation. The coefficient of absorption  $k$  has been assumed to have the same value both for the altered and the unaltered silver bromide. We have, however, experimentally ascertained that this is a fact. It can be easily proved photographically. If, behind a plate, one portion of which has been already exposed so as to yield maximum density, the other portion having received no exposure at all, a very sensitive plate is placed, and if now a suitable exposure be given, it will, on development, be found that the shielded plate has uniform density all over. This proves that  $k$  is the same as regards blue light both for the altered and for the unaltered silver bromide.

The second assumption is that the sensitive film obeys the laws of absorption, as explained at the beginning of this paper. It would prolong this paper very much if we had to furnish here the proof that, as far as the chemically active rays are concerned, and as far as the light *not reflected* is concerned, the law of absorption does hold good. Suffice it to state that, to the more refrangible portion of the spectrum, the sensitive film is as black as Indian ink is to white light.

<sup>1</sup> H.N.—D., p. 83.

To recur to our formula, it requires still more alteration to complete it. The density as given by the formula is the maximum density, and expressed as regards the behaviour of white altered silver bromide towards the blue rays of the spectrum. As we know already, we can develop of that maximum density as much as we please, and the change from white to black during development makes the density more or less equal for all rays of the spectrum. We therefore simply multiply the equation by a constant to express this change, and we call this the development constant. The formula then stands—

$$D = \gamma \log_e [O - (O - 1) \beta^k (1 - a) \frac{It}{e}]$$

$k$ ,  $a$  and  $e$  represent physical and chemical properties of the bromide or silver, which together constitute its sensitiveness to light. We combine them into one single symbol, and write  $i = \frac{e}{k(1 - a)}$ , so that we have finally—

$$(2.) D = \gamma \log_e [O - (O - 1) \beta^i \frac{It}{i}].$$

This formula<sup>1</sup> represents the density after development as a function of the opacity of the unexposed plate, of the exposure, and of the symbol  $i$ , which is a measure of the slowness of the silver bromide, and which symbol we shall call the "inertia" of the silver bromide.

To show the approximation of densities calculated by this formula to those obtained in Experiments 21 and 22, we append here the calculated and the observed densities. For this purpose the plates used for Experiments Nos. 21 and 22 were investigated for their opacity to the rays of the spectrum from F to H, and this opacity was found to be 332.

#### *Experiment 21 compared with theory.*

Exposure, C.M.S.	Density found.	Density calculated.	Exposure, C.M.S.	Density found.	Density calculated.
0.625	.045	.035	80	1.010	.992
1.25	.055	.065	160	1.270	1.272
2.5	.085	.121	320	1.555	1.531
5	.175	.214	640	1.885	1.780
10	.250	.339	1,280	2.088	2.022
20	.460	.520	2,560	2.262	2.218
40	.755	.743	5,120	2.352	2.352

<sup>1</sup> H.N.—B., pp. 155, 159.

## Experiment 22 compared with theory.

Exposure. C.M.S.	Density found.	Density calculated.	Exposure. C.M.S.	Density found.	Density calculated.
1	.060	.092	128	1.875	1.800
2	.160	.172	256	2.290	2.165
4	.340	.302	512	2.535	2.518
8	.500	.482	1,024	2.985	2.860
16	.715	.735	2,048	3.115	3.138
32	.940	1.050	4,096	3.280	3.328
64	1.345	1.405	8,192	3.405	3.405

On examining the "calculated" series of results it will be found that they have exactly the same characteristic properties as those we pointed out as appertaining to the three periods. For the short exposures the calculated densities are nearly proportional to the exposures, whilst from 16 C.M.S. to 1,200 C.M.S. the densities increase by nearly equal amounts for every successive double exposure, and differ very little from densities calculated by the simple formula—

$$D = \gamma [\log. It - C].$$

In order that this may be very clearly seen we append another table comparing in column 1 the densities obtained by the correct formula (2), with densities in column 2 calculated by the approximate formula—

$$D = 1.176 [\log. It - 0.579].$$

Exposure. C.M.S.	(1) Density by correct formula.	(2) Density by approxima- tion.	Exposure, C.M.S.	(1) Density by correct formula.	(2) Density by approxima- tion.
16	.735	.735	256	2.165	2.151
32	1.050	1.089	512	2.518	2.505
64	1.405	1.443	1,024	2.860	2.850
128	1.800	1.797	2,048	3.138	3.213

We think it necessary to draw attention to this agreement, because the approximate formula is extremely easily applied, whilst the correct formula requires very tedious calculations, and we shall make a very important practical application of such calculations.

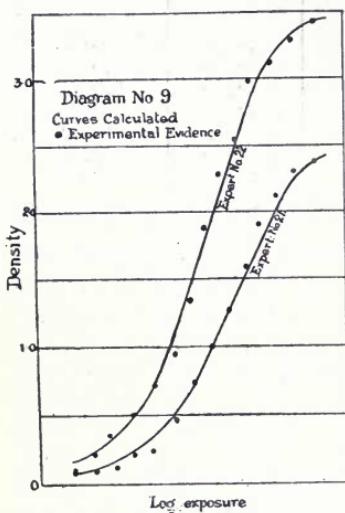
Although there is a close general agreement between the experimental results and the numbers calculated by means of the equations, yet in individual cases there are discrepancies. Diagram No. 9 shows the theoretical curves in full lines, the actual observations being indicated by dots. This diagram leaves little doubt that the action of the light on the sensitive film is fairly represented by our equation, and consequently it may be assumed as proved that the action of the light at any moment is proportional to the amount of light absorbed by unaltered silver bromide.

Nevertheless, we felt that more experimental proof was wanted to support our equation, which represents the resulting density as a function of the opacity of the unexposed plate to blue light. When it is remembered that the density of the unexposed plate is proportional to the silver bromide spread over its area, it will be perceived that this statement means, in fact, that the density of the image depends upon the amount of silver on the plate in some way, and this is almost a self-evident proposition.

We prepared sensitive plates of different opacities by spreading on equal areas different amounts of silver bromide. These plates were measured to ascertain their opacity to blue light, and the following results obtained :—

Plates No. 1.	Amount of silver bromide per 100 sq. cm.	Opacity to blue light.
1	Grms. 0.016	1.738
2	0.031	3.00
3	0.062	10.0
4	0.124	83.0

By means of these opacities four curves were calculated, which are represented in Diagram No. 10. To ascertain whether the relative distances between those curves were true, points in each curve belonging to the same exposure (or abscissæ) had to be determined in at least two different portions. For this purpose four plates, one of each opacity, were simultaneously exposed, and two different exposures were given of 30 and 240 C.M.S. respectively. The



plates were then developed and the ratios of the densities were taken alone for comparison.

The following results were thus obtained :—

Exposure.	Plate I.	Plate II.	Plate III.	Plate IV.	
30 C.M.S.	.. ..	Density. ·065	Density. ·095	Density. ·260	Density. ·272
240 C.M.S.	.. ..	·120	·275	·700	·852
Ratio ..	.. ..	1·84	2·89	2·69	3·31

The ratios which are obtained for the theoretical densities, calculated by the equation (2), are the following ones :—

—	Plate I.	Plate II.	Plate III.	Plate IV.
Ratio .. .. ..	1·70	2·50	2·83	3·22

It will be seen that the theoretical ratios agree as well with the observed ratios as could possibly be expected from so difficult an experiment. In Diagram No. 10 the relative distances of the curves, as calculated from the ratios obtained by the experiment, are marked by dots.

Diagram No. 10 is worthy of some remarks. It will be at once perceived that the more thinly the plates are coated the shorter is that portion of the curve which is a straight line. This means that the period of correct representation is very short, and great contrasts cannot be truly rendered by a thinly-coated plate. It will also be found on closer inspection that the centre of the straight portion is in each curve in a different place, and that the thinner the plate the shorter is the exposure necessary to reach the centre portion. This means that a thinly-coated plate is somewhat faster than a thickly-coated one, though they are made of the same emulsion. A thinly-covered plate, however, appears very much faster than it is in reality. It is incapable of rendering wide contrasts, and



hence the negative always looks flat, and thereby gives to the eye the impression of over-exposure.

We have now learnt the great influence which the opacity of the unexposed plate has on the density of the resultant image, and we must now point out a most important source of error in photographic experiments such as we have described.

If a plate be not perfectly evenly coated, the densities, after development, arising from equal exposures will be different on different parts of that plate. We give here an example of a plate, not a bad one either, on which, in different parts, different exposures were given. The table shows the densities which the same exposure produced on the one half and on the other half of the plate :—

Exposure.	I.	II.	Ratio.
	Density.	Density.	
10	.275	.240	1.14
20	.535	.480	1.12
40	.825	.775	1.06
80	1.185	1.080	1.10

The errors on this plate amount to from 6 to 14 per cent., owing to unequal thickness of the film. It is needless to say that in the dark room, in ruby light, such differences in the thickness of the film cannot be observed. The only remedy for this is to use only very thickly coated plates. We may here say that for our most important experimental work we used slow plates specially prepared for us by Mr. Chapman, of Manchester, every care being taken to secure a thick and even film.

Thickly-coated plates give also very much greater latitude in exposure. The plates used in experiments 21 and 22 would have given good pictures of subjects with contrasts varying from 1 : 80, though the exposures had varied from 1 : 2, so that an exposure of 10 seconds, or one of 20, would have resulted in but little difference in the negatives, excepting that the one would have been much slower in printing, because generally denser. Thinly-coated plates, on the other hand, need very accurately-timed exposures.

#### VI.—SPEED OF SENSITIVE PLATES.

We gave two formulæ as the result of our investigations ; one of them, the approximate one, is the direct result of our experimental work, the other is the mathematical expression of the idea that a certain definite amount of energy is needed to bring a particle of silver bromide into the condition in

which it can afterwards be developed, and that it is only to the light absorbed by unaltered silver bromide that increase of density consequent on increased exposure is due.

Whilst the approximate formula is never strictly true, and can be used only for exposures which fall within the period of correct representation, it is extremely simple, and we are about to describe an important application of it, viz., the determination of the speed of the sensitive plate.

The more correct formula cannot be used for practical applications, owing to its complication, but it serves to indicate the limits within which the approximate formula may safely be used.

In the formula<sup>1</sup>—

$$D = \gamma \cdot \log. \left( O - (O - 1) \beta \frac{It}{i} \right)$$

we may replace  $(O - 1)$  by the symbol  $O$  when that represents a large number, that is, when the plate is richly coated with silver bromide. If, in addition, we remember that  $\log_e \beta$  is  $-\frac{1}{O}$ , the equation can be transformed into another viz. :—

$$D = \gamma \cdot \log. \left( \frac{It}{i} \right)$$

which equation holds good only when the numerical value of  $\frac{It}{i}$  is greater than 1 and less than the opacity  $O$ .<sup>2</sup> It is between these two limits only that this equation gives tolerably correct results. Comparing this last equation with the approximation we gave before, it will be seen that the constant  $C$  of that approximate formula is the logarithm of  $i$ , the symbol measuring those properties of the film which together constitute its sensitiveness, and which we termed the inertia of the plate.

Supposing we had two richly-coated plates, with different inertias,  $i$  and  $i_1$ , and we wished to impress the same density upon them by a given intensity of light  $I$ . They would require different exposures, and the exposures would have to be such that—

$$\frac{It}{i} = \frac{It}{i_1}$$

or the times would have to be chosen so that—

$$\frac{t_1}{i_1} = \frac{t_0}{i_0}$$

<sup>1</sup> H.N.—B., p. 156.

<sup>2</sup> H.N.—B., pp. 63, 156.

This means that if the values of  $i$  are known for different plates, the exposures required to obtain the same results are also known for those plates, if the exposure is known for any one of them.

The determination of the numerical value of the symbol  $i$  is therefore an important problem.

Since the density of the image is an abstract number, it follows that the ratio  $\frac{I_2}{i}$  is an abstract number also, and that  $i$  is therefore an exposure. We termed this symbol the inertia, and it really measures that exposure which will suffice to change a particle of silver bromide into the developable condition. But for its practical application it has another meaning. It measures the least exposure which will just mark the beginning of the period of correct representation.

The speed of the plate is the inverse value ; the longer the exposure needed to bring the plate just to the beginning of the period of correct representation the slower is the plate. Therefore we measure the speed of the plate by the value  $\frac{1}{i}$ .

The method we adopt for measuring the value of  $i$  is briefly as follows :— We give to the plate at least two exposures falling within the period of correct representation, and develop.<sup>1</sup> We then measure the densities exclusive of fog. We thus obtain two equations connecting the two densities  $D_1$  and  $D_2$ , with the two known exposures  $E_1$  and  $E_2$ , viz. :—

$$D_1 = \gamma \log. \frac{E_1}{i} \text{ and } D_2 = \gamma \log. \frac{E_2}{i}$$

from which we obtain by elimination—

$$\log. i = \frac{D_2 \log. E_1 - D_1 \log. E_2}{D_2 - D_1}$$

and—

$$\gamma = \frac{D_2 - D_1}{\log. E_2 - \log. E_1}$$

The value of  $i$  is expressed in candlemetre-seconds, and can be found by reference to ordinary tables of logarithms.

We will now describe our practice. For the determination of the inertia only the central portion of the plate should be used ; the margin should be avoided, as it is liable to be irregular in thickness of film. In order to insure at least two exposures falling within the period of correct representation we give to the plate eight different exposures of 2.5, 5, 10, 20, 40, 80, 160,

<sup>1</sup> D.N.—O., p. 13. H.N.—B., pp. 63, 71.

and 320 C.M.S., leaving a portion of the plate unexposed. We develop this plate with ferrous oxalate, and, after properly washing, fix in a perfectly clean bath of thiosulphate. We then wash and dry spontaneously or by means of alcohol. The length of time for development is judged by the density of the image. We avoid too great density, but develop sufficiently long to obtain a decided deposit for the lower exposures. When all the densities have been measured we subtract from every one of them the density of the fog strip in order to obtain densities "exclusive of fog."

From this series of densities we may calculate the value of  $i$ . For that purpose we find the differences between the consecutive densities, and we choose from the series those points which give differences most nearly alike. As an example we quote the series of results obtained with the Manchester slow plate of experiment No. 21:—

Exposures .. ..	2.5"	5"	10"	20"	40"	80"	160"
Densities .. ..	.085	.175	.250	.460	.755	1.010	1.270
Differences .. ..	.09	.075	.210	.295	.255	.260	

We should take the results of exposures from 20 C.M.S. to 160 C.M.S., as those falling within the period of correct exposure. Choosing the exposures 20 and 160 for the calculations, we should obtain, in accordance with the formula given—

$$\log. i = \frac{1.270 \times \log. 20 - 0.460 \times \log. 160}{1.270 - 0.460}$$

or  $\log. i = 0.787$ , and from an ordinary logarithm table we should find  $i = 6.12$  candlemetre-seconds.

In another experiment with a plate of the same make the following results were obtained:—

Exposures .. ..	10"	20"	40"	80"
Densities .. ..	.300	.590	.910	1.260
Differences .. ..	.290	.320	.350	

Choosing only the 20" and 80" points, we have—

$$\log. i = \frac{1.260 \times \log. 20 - 0.590 \times \log. 80}{1.260 - 0.590} = 0.771$$

or  $i = 5.90$  candlemetre-seconds.<sup>1</sup>

It will be seen that these values for the inertia of the "Manchester Slow" plate are almost alike. With faster plates it is not so easy to obtain quite such

<sup>1</sup> Correspondence:—Driffield—Cowan, 25th July, 1892.

concordant values, but they are always sufficiently accurate for practical purposes, for whether an exposure in practice be four or five seconds it will not appreciably alter the resulting negative, so that in the determination of the inertia an error of 10 per cent. is fortunately not of very great consequence, and in most cases two determinations carefully made will not differ more than 10 per cent.

We prefer, however, to obtain the result by a graphic method, by means of which we avoid all calculations and all references to tables of logarithms. We scratch on an ordinary slate a horizontal scale of inertias similar to the scale of an ordinary slide rule, but we repeat the scale four times instead of twice, as in the case of the slide rule. Diagram No. 11 shows this arrangement. We scratch at points 2.5, 5, 10, 20, 40, 80, 160, and 320 of this scale vertical lines (exposure lines), and divide them each into 20 equal parts, marking the highest as density 2.0, the lowest as 0. Having measured the densities we mark them on the scales of the corresponding exposure lines, and draw a straight line through those points which appear to fall most accurately within such a line. It is better to stretch a white thread across these points, as the portion of the line can thus be more easily determined. Where the thread or the straight line intersects the inertia scale we can at once read off the inertia of the plate.

The solutions of the problem of ascertaining the inertia or its inverse the speed of the plate have hitherto been unsatisfactory, and always depends finally upon the judgment of the comparative visibility of letters or numbers printed upon a sensitive plate.

Our method, by referring the speed to a standard candle as unit will enable different operators to obtain almost identical and definite numerical results. Should at any time a better practical unit of light be found, the method is at once applicable with it also. The fact is, we have based our method on the measured effects produced by a given unit of light, excluding the influence of alterations in development, whilst the present method, by means of Warnerke's sensitometer, depends entirely upon development. We could so alter the composition of the developer as to make a rapid plate give most misleading results.

Such a proceeding is impossible with our method.

There is a theoretical possibility that a plate may be rapid to one developer and slow to another, so as to require different exposures according to the developer used. If silver bromide be reduced to metallic silver, 22,700 units of heat must be supplied to replace the heat of combination. Of this amount of heat the developer in the act of development supplies a portion. Ferrous oxalate, for instance, would probably supply 12,900 units, so that the light

need only supply the difference, viz., 9,800 units. But if another developer could supply more than 12,900 units, then the light, clearly, need not supply quite so much, and in that case the plate would be faster to one developer than to another.

We have not paid such close attention to this question yet as to enable us to decide it finally, but as far as our experiments have gone we have found very little difference, if any, between the various developers, and we do not feel justified in assigning to the small differences we have observed any great importance.

If a developer could be found which would render a plate materially faster, that developer would strike a serious blow at the hypothesis that the latent image consists of sub-bromide of silver.

We append a number of interesting diagrams representing our graphic method of determining the inertia of a plate.

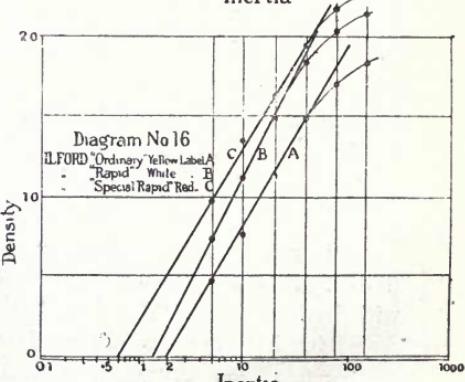
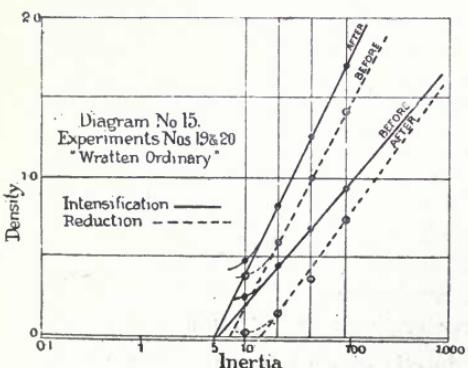
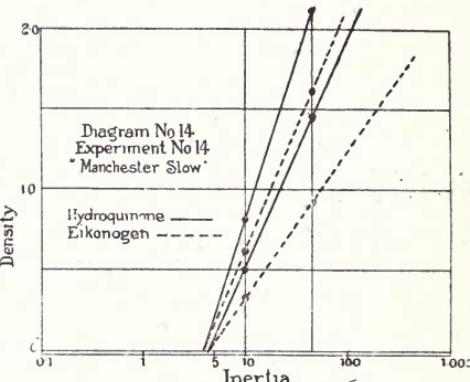
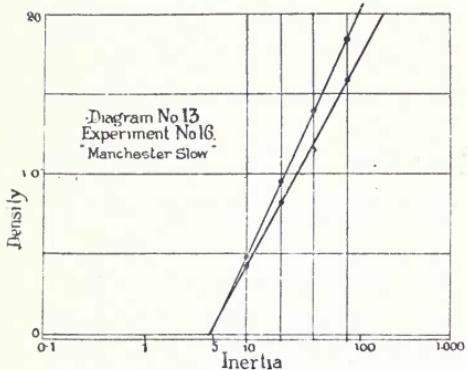
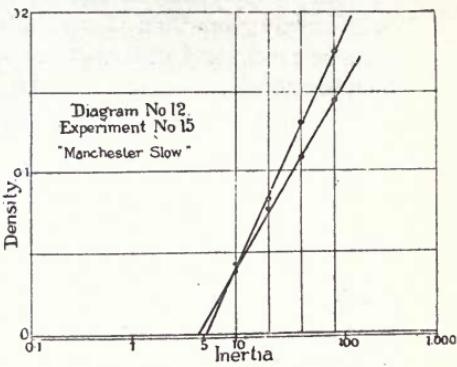
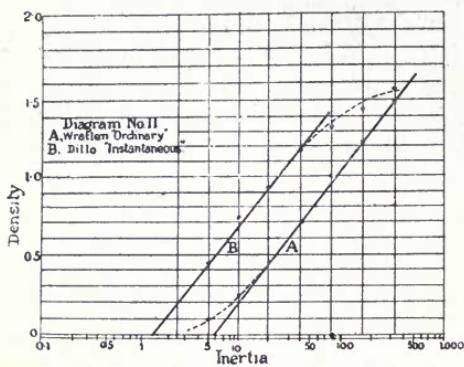
Diagram No. 11 shows the general arrangement we adopt for finding graphically the value of the inertia. An ordinary "slide rule" furnishes the mode of subdividing the scale (the distances of the numbers being proportional to their logarithms). The two curves are the curves of Wratten and Wainwright "ordinary" and "instantaneous" plates. It will be noticed that the "instantaneous" plate shows, within the given exposures, a portion of the period of over-exposure, whilst the "ordinary" shows a portion of the period of "under-exposure." The inertia of the one is 1.4, that of the other 5.5, and in round numbers the one plate is four times as fast as the other.

Diagram No. 12 shows the results of experiment 15 graphically, for the purpose of showing that variations in the mode of development do not influence the determination of the inertia; the densities of the two modes of development being different, yet the straight lines practically converge to the same point.

Diagram No. 13.—This diagram represents another variation in pyro development, viz., in the amount of bromide (experiment 16). It will be again seen that the values of the inertia are almost identical, in spite of a considerable difference in the composition of the developer and the time of development.

Diagram No. 14 shows four determinations of the inertia of one plate (see experiment 14), two determinations being made with eikonogen and two with hydroquinone. The duration of development being different for each determination, yet the results of all four determinations are practically identical.

Diagram No. 15 shows that the inertia of a plate can be determined after intensification, *but not after reduction*. It is, therefore, better to develop



too little rather than too much. We clearly must not resort to reduction, but we may intensify if the trial plates have been under-developed. (Experiments 19 and 20.)

Diagram No. 16 shows the determination of inertia of the Ilford plates, "ordinary," "rapid," and "special rapid" (red label). Their inertias are respectively 2.0, 1.4, and 0.56, and their speeds are relatively as 1 : 1.41 : 3.5. The "red label" plates are the most rapid plates we have so far investigated, but we found it very difficult to ascertain their true speed in the camera, on account of the difficulty in securing adequate density.

When the inertia of the plate is known, it is possible to time the exposures in the camera so that the densities of the gradations are almost exactly proportional to the logarithms of the light intensities which produced them. By this means negatives can be produced which satisfy very nearly the definition we gave of a theoretically perfect negative. It must be borne in mind, however, that such a negative is not necessarily true to nature. The optical density after development differs from the density of the latent image. If the negative is to be true to nature, a plate must be used which is richly coated, the exposure must be carefully timed, and the development must be carried only so far that the value of the development constant  $\gamma$  is numerically equal to 1. Experiments which we have made indicate that for the production of artistic effects on ordinary silver chloride paper, it is necessary to exaggerate the densities, *i.e.*, to prolong the development until  $\gamma$  is greater than 1, and nearly reaches the value 2. This requires further investigation; suffice it to have pointed out that what Captain Abney terms "photographic untruth" is not necessarily inherent in photography, since the photographer has it in his power to decide the degree of exaggeration.

The exposure to be given in the camera can be found by means of the actinograph,<sup>1</sup> when the inertia of the plate is known.

The "actinograph speed" of the plate is found by means of the formula  $S = 34/i$ , where  $S$  is the speed and  $i$  the inertia in candlemetre-seconds. We find, for instance, the speed of the Ilford plates from their inertia (as shown on Diagram 16) :—

						Speed.
Ilford "ordinary" .. .. .. ..	=	$\frac{34}{2}$	=	17		
Ilford "rapid" .. .. .. ..	=	$\frac{34}{1.4}$	=	24		
Ilford "special rapid" .. .. .. ..	=	$\frac{34}{0.56}$	=	60		

<sup>1</sup> See *J.S.C.I.*, 1890, 370, or the Photographic Societies' Reporter for 30th April, 1889.

This method of referring the sensitiveness of the plate to the candlemetre-second as unit will, we believe, greatly promote progress both in the preparation of the plates and in their application. We flatter ourselves that we have supplied one of the greatest needs of plate makers and photographers in general, by enabling them, for the first time, to ascertain accurately the sensitiveness of different plates, and by means of the actinograph to apply this information in practice.

The above is the main practical result which has accrued from our investigations, but, incidentally, we have shown the fallacy of many popular views on the subject of development, and the paramount importance of correct exposure.

From a purely scientific point of view, perhaps, the most interesting result of our labour is the elucidation of the numerical relation between the exposure and its effect on the sensitive film, and the simple explanation of these relations, based upon the optical properties of the unexposed sensitive film. It would not have been difficult to extend these considerations so as to include in them the reversing action of the less refrangible rays. This would not, however, have served any practical end at present, and it would have complicated the formulæ very considerably. We reserve for a future communication this extension of the law which we have discovered.

*Reprinted from the Journal of the Society of Chemical Industry, 31st July,  
1890, Vol. IX., page 722.*

## COMMUNICATION ON THE ACCURACY OF THE GREASE- SPOT PHOTOMETER FOR MEASURING THE DENSITY OF PHOTOGRAPHIC PLATES AND A NOTE ON THE SECTOR PHOTOMETER

BY

CAPTAIN W. DE W. ABNEY, C.B., R.E., D.C.L., F.R.S.

---

THE publication of a paper by Messrs. Hurter and Driffield in the *J.S.C.I.*, on "Photo-chemical Investigations and a New Method of Determination of the Sensitiveness of Photographic Plates," has induced me to offer a few criticisms on the subject.

I have two reasons for doing this. One is that I have written a good deal regarding part of it, and the other that some doubt is thrown in the paper on the accuracy of the results I have obtained, owing, it is asserted, to the photometer I use being faulty.

I should have been unwilling to enter into a criticism of the paper now the season is over were it not that it will no doubt be largely quoted at home and abroad as giving an authoritative exposition of the law of density, and that no opportunity of having a say in the matter would occur before November.

We may take the paper as practically divided into four parts:—Definition of terms employed; instrument for measuring and method of measuring the density of deposit in photographic plates; methods of producing density; and a mathematical investigation of the subject.

Under the first heading I may have one or two criticisms to make subsequently—such as on the law of absorption applied to a film in which opaque

particles are embedded—but for the present I wish to confine myself to the second division, viz., the instrument and the mode of measuring densities, for, if these are in fault, the measured densities and the application of theory to them will require revision.

To begin with the instrument itself as used by the authors. There is a statement made regarding the method of photometry employed to which I must take exception, and that is that the Bunsen disc is more sensitive than the (Rumford) method of shadows. The leading authorities on photometry in London, viz., the Gas Referees, have adopted the shadow test, and certainly the measurements made by Mr. Vernon Harcourt are not wanting in delicacy. The well-known drawback to the grease-spot method is the necessity of excluding all reflected light from the grease spot, and when it is recollected that the blackest lampblack reflects more than 2 per cent. of white light, the exclusion of all reflected light becomes a problem very hard to solve, more especially in an instrument 12 by 4 by 6 inches, such as used by Messrs. Hurter and Driffield. I am not saying that they have not overcome this difficulty, but I bring forward a possible objection to this instrument. This may be passed over, however; but, unless I am very much mistaken, a much more serious, if not fatal, objection must be taken to it when measuring the density of photographic deposits, and is one I have long been practically acquainted with, and which I have again investigated recently. Let anyone, after focussing a view, replace the ground glass of a camera by a photographic negative, and place his head under the focussing cloth. He will see two objects, the lens through the plate and the view, more or less dim, on the negative itself. In other words, the film acts like ground glass and is partially translucent. Now, if the negative be replaced by a glass of apparently the same darkness, in which the colouring matter is part of the glass itself, the view is no longer visible, or, if visible at all, very faintly so, but the lens will be clearly seen. Now, ground glass, if illuminated, becomes practically a source of light, the light being scattered in every direction, but it naturally illuminates more strongly in the direction from which the original light falls on it, if the glass be perpendicular to that direction. Thus, when a piece of ground glass is placed at the end of a narrow tube, which is inserted in the walls of a dark and black-painted room (the ground surface being inside the room), it will be found that if a beam of light be sent through the tube, not only is the room illuminated exactly opposite the tube, as it would be were the ground glass removed, but also at every angle with the axis of the tube. The illumination of a white surface gave the following results in one case, the surface being always at the same distance from the aperture.

TABLE I.

Angle from axis. Deg.									Relative illumination.
0	..	..	..	..	..	..	..	..	100
10	..	..	..	..	..	..	..	..	64
20	..	..	..	..	..	..	..	..	21
30	..	..	..	..	..	..	..	..	14
40	..	..	..	..	..	..	..	..	8.2
50	..	..	..	..	..	..	..	..	7.2
60	..	..	..	..	..	..	..	..	6.0

Evidently the amount of scattered light would have to be taken into account, as, if not, it would be immaterial if the ground glass were in front of the tube or not, except for the small amount of light which would be reflected back towards the source of light; and, further, the brightness of the light which illuminated the grease spot would not vary exactly inversely as the square of the distance, since the light is not symmetrically scattered, if we may use such a phrase.

If the ground glass in the above experiment be replaced by a piece of a negative the same scattering of light will be readily seen by holding a piece of white card about 1 foot from the orifice.

Now, let us see how the results obtained by the instrument under consideration would be affected by the "ground glass" effect of the negative. Suppose we have two lights properly enclosed in a darkened room, one being stationary, with an aperture in front of it, the flame being of such dimensions that it more than fills the aperture (in fact, just as the authors arrange both their lights) and the other movable. Let a movable Bunsen disc be placed at some fixed distance from the aperture, and the other light be moved till equality of illumination of the grease spot is secured, and let the distances of the aperture and of the movable light from the grease spot be noted. Next, let the Bunsen disc be moved to a different distance from the aperture and the movable light be again moved till equality of illumination is secured, and let the two distances be again measured. The distances of the aperture and of the movable light from the grease spot, in the first case, should be proportional to the two distances in the second case. Suppose, in the first instance, the distance of the aperture from the grease spot was 6 inches, and that of the movable light 3 feet, then, if the grease spot be moved to 12 inches from the aperture, the distance of the movable light should be 6 feet, and so on. Now, if the measurement of density of a plate by the grease-spot method be correct when a film is placed in contact with the aperture, the same should hold good, but if the scattering of light by the film affects the

result it should not. To test this, I have made a good many very careful experiments, and I cite one here which is a sample of the results obtained in all cases. The plan adopted was to make measures of a lighted aperture as stated, and then, without any alteration of the general arrangement, to place a portion of a plate with a photographic deposit on it against the aperture, and measure the light coming through it by placing the grease spot at different distances from the aperture, and then to get equality of grease-spot illumination by moving the second light. Table II gives the measures of the unmarked aperture, which was about  $\frac{1}{4}$  inch in diameter as taken.

TABLE II.

Distances of Aperture from Grease Spot.	Distance of Movable Light from Grease Spot.		
	Readings.	Mean.	Adopted.
C.M.			
3.5	4, 3.75, 4.2	4	4
7	8, 8, 8	8	8
14	16, 16	16	16
28	31.5, 31.5, 32	31.7	32
42	47.5, 48.5, 48.5	48.2	48
56	63, 64, 63	63.3	64
70	80, 78, 79, 79	79	80

The readings are sufficiently close to show that for naked lights the results are concordant. Table III gives the measures of the light passing through a negative, and at different distances reaching the grease spot.

TABLE III.

Distance of Aperture from Grease Spot Negative in Front.	Distance of Movable Light from Grease Spot.			Ratio of Distance of Aperture and Movable Light from Grease Spot,
	Readings.	Mean.	Adopted.	
C.M.				
3	42.5, 42, 42.5	42.7	42.7	14.2
4	48, 49, 49	48.7	48.7	12.2
5	57, 58, 56.5	57.2	57.2	11.4
6	63, 62, 64	63	63	10.5
8	84, 85, 84	84.3	84.3	10.5
9	93, 95, 95	93.7	93.7	10.4
10	102, 99, 100	100.3	100.3	10.03

If we critically examine this table we shall at once notice that large discrepancies appear. For instance, at 6 in the first column the distance of the movable lamp should be double that at 3, or it should be 85·4, but it is only 63; so at 8, if it were double that at 4, it should be 97·4, whereas it is 84·2; at 10 it should be double that at 5, or 114·4, whereas it is 100·3. The last column gives the ratios of the distances.

The squares of the ratios of the first and last measures, *viz.*, at 3 and 10, the distances of the aperture from the source are as 201·6 to 100·6, or nearly 2 to 1. The nearer distance of the screen to the aperture therefore gives a lower value of the transmitted light than the further one. The question is which, if either, is correct, and, looking at it from a theoretical point of view, it appears that neither is. According to the two measures, the light transmitted through the negative was about one hundred and fifty-fourth and one seventy-seventh, whereas by a correct means of measurement the amount transmitted was found close upon one-fortieth.

The trial of their instrument by the authors with Indian ink and indigo solution is totally different to its trial with films. In a minor degree Indian ink scatters, but the indigo solution is transparent. Now, from the published description of the instrument as used by Messrs. Hurter and Driffield, it is probably impossible for the grease spot to be nearer to the aperture than 1 $\frac{1}{4}$  inches, or about 3 cm., seeing that the inner box is 2-inch cube and that we have to add for the thickness of the glass of the negative and the thickness of the box itself. We may take it that the distance of the grease spot in the measures made varies between 6 inches and 1 $\frac{1}{4}$  (15 and 3 cm.) inches, and in this range there can be a remarkable variation of densities to be obtained from the different readings. It may be said that the measures obtained are concordant one with another. This may be so, since it will be seen from Table III that after a certain range is passed, the ratios of the two distances become almost the same, but they will not be true measures of the light transmitted. Taking all things into account, it seems not unreasonable to conclude that the measures of light given as transmitted through deposits are too small; and, as has been shown, when the densities are great and the grease spot has to be moved close to the aperture, the variation may be as great at 100 per cent. less than would have been obtained if a longer box had been employed and the disc were further away from the aperture.

In this part of the paper to which I am confining myself the authors allude to the photometer which I use, and which works on the principle of cutting off light by rotating sectors of varying apertures, but a remark is made which more than suggests a want of accuracy in its measure. The authors say that with it the density measured "rises to over 100 per cent.

(of error) with plates of high densities, which renders it utterly untrustworthy." From the formula of light transmitted through my photometer given by the authors the 100 per cent. evidently means making the density too great. In taking exception to the results obtained by their grease-spot method, I have indicated experiments which anyone interested can try, and I shall now give some made with my own photometer. I might stop here and use an "*argumentum ad hominem*," which would be thus:—The grease-spot photometer having been proved capable of giving results *inter se* 100 per cent. in error and mine having in the same hands given results 100 per cent. in error when compared with them, may it not be assumed that my photometer gives correct results, or, at all events, more nearly correct results than the grease-spot method gives? Setting this kind of argument on one side, I will for a brief space examine the statements that have been made regarding my photometer.

They say the light transmitted is more correctly represented by—

$$I_x = I \frac{\phi}{360^\circ} + C$$

(when  $I_x$  is the light transmitted,  $I$  the light falling on the sector,  $\phi$  the aperture of the sector, and  $C$  a constant), than by—

$$I_x = I \frac{\phi}{360^\circ}$$

which I have always taken as the true transmission. Their formula, of course, if pushed to extremes, results in an absurdity, for, if the aperture be  $0^\circ$ , that is, if the sectors be closed, still  $C$  light will be transmitted. The reason assigned for adopting this formula is said to "be due to the semi-shadow on both edges of the sector openings." Evidently, then, if we increase the number of these openings, keeping the total aperture the same, the magnitude of  $C$  will increase. If with two sectors it is  $C$ , then with four sectors it will be  $2C$  and with eight sectors  $4C$ , and so on, till we arrive at a point when  $nC = 1$ , which is the total intensity, leaving no light to pass through the apertures. Had the formula been—

$$I_x = \left( I \frac{\phi}{360} - C \right)$$

there might have been something to say in its favour, for, if the light be close to the sectors, the thickness of the metal of which the sectors are made might possibly cut off a fraction of a degree, but, as I never use the photometer in such a manner, any error caused by this is quite negligible, more especially as the photometer, for other reasons, is rarely read below  $7^\circ$  or  $8^\circ$ , the light being adjusted to make higher readings when low readings with one position of the light would be obtained.

I may as well here give some experimental results of the correctness of the photometer. Two incandescent lights, approximately similar in dimensions, were used and kept glowing with a constant current. One lamp was fixed at a distance of about 18 inches from the screen, the other placed on a block sliding on a bar, and the illuminated shadows cast by a rod fell on a white patch, and were equalised in brightness. The rotating sectors were introduced between the first light and the screen and were fixed at different apertures. Equality of illumination was obtained by sliding one light along the bar. The following are the results:—

TABLE IV.

Sector Set at.	Mean Reading of the Distance of the Movable Lamp.	Calculated Value.
°		°
180	16.25	180
90	23	90
46	32	46.5
20.5	48.5	20.2
10	69	10
4.8	101	4.7

In the next two tables we have a large luminous source, viz., an Argand burner  $\frac{3}{4}$  inch in diameter.

The first shows the worst measures made and the second one usually obtained:—

TABLE V.

Sector Set at.	Mean Readings of Lamp from Source.	Calculated Intensity.
°		
180	37.75	176.8
88	19.5	88
60	23.5	60.5
45	27.25	44.5
30	33	30.8
10	59	9.6
5	83	4.8

TABLE VI.

Sector Set at.	Mean Reading of Lamp from Source.	Calculated Intensity.
180	13.25	180
90	18.75	90.3
44.5	24.75	44.6
10	57.25	9.6
5.2	79.0	5.1
3	196.5	2.8

Equally good results were obtained when the sectors were placed in the beam of light, which was focussed on the screen by means of a lens.

In the foregoing remarks I have given my criticisms on the accuracy of the grease-spot photometer for measuring densities, and it has seemed to me that the whole paper more or less hangs on this. I have also endeavoured to vindicate the sector photometer from the slur which has been placed upon it. All the experiments I have given on both subjects are easy to repeat, and I trust that some independent physicist will take the matter up and judge between myself and the authors.

It would be premature to go into the proofs which can be adduced that the method employed by myself for measuring densities is correct. If necessary, such proof can be given. Doubt has only been thrown on the instrument I use, and not on the manner of using it in its latest development. My admiration of the paper is not diminished by any fault I have found in the methods employed by Messrs. Hurter and Driffield, but I thought it right in the interests of photographic science to point out what I believe to be a weak spot in the proofs of their theory.